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Studies on Metal Complexes of Isocytosine Derivatives: The Crystal Structure of Copper(II) Complex of 2-Hydrazino-4-hydroxy-6-methylpyrimidine[1]

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The crystal structure of the copper(II) complex of 2-hydrazino-4-hydroxy-6-methylpyrimidine (LH) has been determined from three-dimensional X-ray diffractometer data by heavy atom Fourier methods. Crystals of $[Cu(LH)_2(H_2O)]Cl_2 \cdot 2H_2O$ are triclinic with unit cell dimensions $a=10.020(2)$, $b=14.384(2)$, $c=7.205(1)$ Å, $\alpha=104.63(2)^\circ$, $\beta=111.04(1)^\circ$, $\gamma=84.93(2)^\circ$, space group P 1, and $Z=2$. Block-diagonal least-squares refinement using 3126 independent reflections yielded an R value of 0.062. There are two mirror-image complex molecules in a unit cell. Each copper(II) complex has five coordinated bonds and assumes a distorted square pyramid structure. The two ligand molecules, $(LH)_2$ are *trans* coordinated to the copper(II) ion through nitrogen atoms N3 of the pyrimidine rings and also through the amino nitrogen atoms of the hydrazino groups. In each copper(II) complex, the one apical coordination site is occupied by the water oxygen atom. The hydroxyl group at C4 of the pyrimidine ring takes the keto form, since the hydrogen atom of the hydroxyl group transfers to N1 of the ring. The chloride ions are not directly hydrogen bonded to the N1 atoms of the pyrimidine bases, but are bound to the apical water oxygen atoms. The pyrimidine rings in the crystals are not stacked in parallel but are inclined at an angle of 18.9 or 18.8°.

Keywords——crystal structure; mirror-image complexes; keto form; Cu; stacking; five coordinated bonds; distorted square pyramid; apical bond; metal complex; pyrimidine derivative

Introduction

It has been suggested that conformation changes in metalloenzymes such as deoxyribonucleic acid (DNA) polymerase I, can often be produced by metal ions.[3]

In addition, the stabilizing or destabilizing effects of various bivalent metal ions on DNA have been well established.[4] When copper(II) ions coordinate tightly to the purine bases at low ionic strength (5×10^{-3} M $NaClO_4$, pH 5.6), the DNA double helix is destabilized. On the other hand, small amounts of copper(II) ions coordinate loosely to purine bases at higher ionic strength (0.1 M $NaClO_4$) and cause stabilization of the Watson-Crick base pairing.[5,6]

According to Eichhorn and Shin, copper(II) and cadmium(II) ions bind the bases of unwound DNA in pairs, and because they have relatively high affinity for the bases, they

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continue to bind the bases on cooling, preventing rewinding. The addition of sufficient electrolyte to these solutions brings about rewinding of the double helix.[7]

Since nucleotide bases in the DNA structure have several coordination and hydrogen bonding sites, conformational changes may occur in DNA due to pH change or the presence of some metal ions.

We have demonstrated that adenine has different coordination sites for different metal ions and may act as a unidentate or polydentate ligand.[8-13]

Like adenine, 2-hydrazino-4-hydroxy-6-methylpyrimidine (LH) has several available coordination sites, but the conclusive identification of the coordination sites for various metal ions has proved to be difficult simply by spectrographic methods.[14] Therefore, we carried out X-ray analysis of the zinc(II) complex and demonstrated that the ligand molecule, LH, is coordinated to the zinc(II) ion through the N3 atom of the pyrimidine ring and also through the amino nitrogen atom of the hydrazino group.[15]

2-hydrazino-4-hydroxy-6-methylpyrimidine
(denoted by LH or $C_5H_8N_4O$)

isocytosine

Chart 1

Since the IR and UV spectra of the LH–Cu(II) complex were different from those of the LH–Zn(II) complex, the structures of the copper(II) and zinc(II) complexes of LH were considered to be different.

In the present work, the crystal structure of the copper(II) complex of this ligand(LH) has been determined to identify the structural differences between the two complexes.

Experimental

Preparation of $[Cu(C_5H_8N_4O)_2(H_2O)]Cl_2 \cdot 2H_2O$——$CuCl_2 \cdot 2H_2O$ was dissolved in H_2O in an ice bath, and the ligand LH was dissolved in 1 N HCl. The two solutions were mixed and the resulting blue solution was evaporated under reduced pressure at room temperature. Blue crystals, obtained after several hours, were

Table I. Crystal Data for $[Cu(C_5H_8N_4O)_2(H_2O)]Cl_2 \cdot 2H_2O$

$C_{10}H_{22}Cl_2CuN_8O_5$	F.W.$=468.79$	
Crystal system	Triclinic	
Cell constants	$a=10.020(2)$ Å	$\alpha=104.63(2)°$
	$b=14.384(2)$ Å	$\beta=111.04(1)°$
	$c=7.205(1)$ Å	$\gamma=84.93(2)°$
	$V=937.9(3)$ Å^3	
Space group	P1	
Z	2	
Density (obsd)	$D_m=1.643\ g \cdot cm^{-3}$	
(calcd)	$D_x=1.660\ g \cdot cm^{-3}$	

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Table II. Atomic Parameters

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	2(2)	−6(1)	11(2)	25(1)	26(1)	33(1)	−4(1)	7(1)	7(1)
Cu′	5002(2)	4993(1)	2512(2)	25(1)	26(1)	33(1)	−4(1)	8(1)	8(1)
Cl(1)	−893(4)	1729(3)	5994(5)	41(2)	45(2)	29(2)	−9(1)	6(1)	7(1)
Cl(2)	903(4)	8239(2)	5147(5)	42(2)	45(2)	40(2)	−8(1)	17(1)	14(1)
Cl(3)	4102(4)	3242(2)	6742(5)	42(2)	43(2)	34(2)	2(1)	9(1)	18(1)
Cl(4)	5902(4)	6730(2)	9384(5)	41(2)	45(2)	37(2)	3(1)	19(1)	10(1)
O(0)	−2(11)	8(8)	3080(15)	43(5)	68(6)	37(5)	9(4)	18(4)	23(5)
N(1)	4304(9)	494(7)	2004(14)	11(4)	25(5)	34(5)	−1(3)	6(4)	8(4)
C(2)	2879(11)	484(7)	1311(15)	21(5)	22(5)	20(5)	4(4)	11(4)	8(4)
N(3)	2079(9)	−273(13)	773(13)	20(4)	20(4)	22(4)	−4(3)	9(4)	5(4)
C(4)	2736(10)	−1157(7)	971(16)	13(5)	18(5)	31(6)	4(4)	4(4)	9(4)
C(5)	4288(12)	−1189(8)	1639(19)	23(6)	19(5)	45(7)	0(4)	13(5)	9(5)
C(6)	5045(11)	−370(8)	2166(18)	14(5)	31(6)	35(6)	3(4)	9(4)	10(5)
N(7)	2218(10)	1352(6)	1148(16)	18(5)	16(4)	50(6)	−2(4)	6(4)	12(4)
N(8)	690(9)	1357(6)	514(14)	15(4)	23(5)	28(5)	−4(4)	3(4)	6(4)
O(9)	1997(9)	−1878(6)	595(15)	26(4)	17(4)	62(6)	−3(3)	9(4)	16(4)
C(9)	6638(12)	−323(10)	2860(21)	15(5)	42(7)	49(7)	5(5)	5(5)	19(6)
N(11)	−4314(9)	−491(7)	−2808(14)	12(4)	25(5)	31(5)	0(3)	4(4)	8(4)
C(12)	−2866(11)	−490(7)	−2073(15)	25(5)	17(5)	18(5)	0(4)	6(4)	8(4)
N(13)	−2067(9)	292(6)	−1032(13)	19(4)	10(4)	20(4)	−2(3)	4(3)	1(3)
C(14)	−2741(11)	1156(7)	−604(16)	18(5)	14(5)	30(6)	0(4)	7(4)	4(4)
C(15)	−4281(12)	1193(8)	−1439(19)	21(5)	28(6)	39(7)	7(5)	5(5)	14(5)
C(16)	−5023(11)	386(8)	−2499(17)	21(5)	23(5)	28(6)	3(4)	3(4)	11(4)
N(17)	−2203(9)	−1360(7)	−2439(15)	16(4)	19(4)	43(6)	−5(4)	3(4)	3(4)
N(18)	−703(9)	−1346(7)	−1561(14)	11(4)	26(5)	33(5)	−5(4)	3(4)	6(4)
O(19)	−1996(8)	1877(5)	482(14)	24(4)	18(4)	47(5)	−4(3)	3(4)	−1(4)
C(19)	−6649(12)	340(9)	−3463(21)	18(5)	36(7)	47(7)	1(5)	8(5)	15(6)
O(0′)	4987(11)	5021(8)	5574(15)	45(5)	59(6)	37(5)	−18(4)	15(4)	8(4)
N(1′)	9310(9)	4509(7)	4011(14)	16(4)	23(5)	33(5)	−3(3)	5(4)	8(4)
C(2′)	7874(11)	4514(7)	3328(16)	21(5)	22(5)	22(5)	−1(4)	10(4)	8(4)
N(3′)	7097(9)	5261(6)	3547(13)	19(4)	17(4)	22(4)	−3(3)	5(4)	5(3)
C(4′)	7744(11)	6168(8)	4642(16)	15(5)	26(5)	24(5)	−6(4)	4(4)	6(4)
C(5′)	9281(12)	6193(8)	5351(19)	20(5)	31(6)	41(7)	−6(5)	12(5)	8(5)
C(6′)	10030(11)	5377(8)	5051(18)	15(5)	29(6)	37(6)	−2(4)	13(5)	5(5)
N(7′)	7225(10)	3638(6)	2310(16)	18(4)	16(4)	46(6)	−3(4)	10(4)	2(4)
N(8′)	5699(9)	3670(7)	1676(15)	14(4)	24(5)	35(5)	−3(4)	6(4)	6(4)
O(9′)	6990(8)	6884(5)	4973(14)	28(4)	18(4)	47(5)	−6(3)	9(4)	−1(4)
C(9′)	11656(12)	5310(10)	5679(21)	16(5)	51(8)	46(7)	−7(5)	6(5)	4(6)
N(11′)	683(9)	5502(7)	195(15)	11(4)	28(5)	32(5)	−3(4)	−1(4)	11(4)
C(12′)	2132(11)	5500(7)	933(16)	17(5)	24(5)	21(5)	−8(4)	2(4)	7(4)
N(13′)	2918(9)	4727(6)	1198(13)	20(4)	14(4)	23(4)	−5(3)	2(4)	8(3)
C(14′)	2266(11)	3825(8)	732(16)	16(5)	30(6)	24(5)	−7(4)	3(4)	9(4)
C(15′)	711(12)	3816(9)	−128(18)	23(6)	31(6)	30(6)	−8(5)	−2(5)	4(5)
C(16′)	−12(11)	4613(8)	−346(16)	16(5)	28(5)	23(5)	−9(4)	−1(4)	7(4)
N(17′)	2790(9)	6366(7)	1447(16)	16(4)	20(4)	47(6)	0(4)	1(4)	13(4)
N(18′)	4308(9)	6348(7)	2316(15)	15(4)	25(5)	35(5)	−3(4)	7(4)	9(4)
O(19′)	3020(8)	3123(5)	1104(14)	24(4)	17(4)	56(5)	−4(3)	5(4)	16(4)
C(19′)	−1631(12)	4687(9)	−1260(21)	16(5)	38(7)	47(7)	−4(5)	4(5)	15(6)
O(1)	5821(9)	2186(6)	3943(14)	32(4)	28(4)	48(5)	−8(4)	6(4)	10(4)
O(2)	−816(9)	7184(6)	631(15)	30(4)	33(5)	49(5)	−1(4)	14(4)	11(4)
O(3)	794(9)	2815(6)	4254(14)	30(4)	31(5)	44(5)	4(4)	8(4)	11(4)
O(4)	4201(9)	7811(6)	5933(14)	32(4)	33(5)	45(5)	−4(4)	10(4)	10(4)

Non-hydrogen atoms. Values are × 10^4. Anisotropic temperature factors are of the form:
$T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$

washed with a little ice-cold water and dried under reduced pressure. The melting point of the product was 226° (dec.).[14]

Crystal Data——The crystals of the complex are blue prisms. The specimen employed for data collection had dimensions of $(0.5 \times 0.4 \times 0.4)$ mm; it was coated with vaseline and mounted on a glass fiber. The crystal data are given in Table I.

The intensities were measured on a Rigaku four-circle automatic diffractometer with monochromated Cu-K_α radiation using a graphite plate. The intensities of reflections with 2θ values up to 150° were collected by the θ—2θ scan method with a 2θ scan rate of 2° min^{-1}. The background was measured at each end of the scan range for 10 sec. The intensities were collected for Lorentz and polarization factors but not for absorption factors. The total number of independent observed reflections above the $2\sigma(F)$ level was 3126 out of 3863 theoretically possible reflections.

Determination and Refinement of the Structure——From an isolated strong peak at $u=0.5$, $v=0.5$, $w=0.25$ on the three-dimensional Patterson map, the two copper(II) ions were placed at (0, 0, 0) and (0.5, 0.5, 0.25). Structure determination was started on the basis of space group P $\bar{1}$, but as seen from the square pyramidal coordination of copper(II) ions, they could not on the center of symmetry. Furthermore, refinement of the centro-symmetric structure proved to be impossible. The pseudo-center of symmetry was eliminated by placing the chloride ions at appropriate positions. Refinement of the structure was carried out by the block-diagonal matrix least-squares method.[16]

Finally, six cycles of least-squares refinement with an anisotropic temperature factor gave an R index of 0.062. In this calculation, anisotropic thermal motions were assumed for 52 atoms and the following weight system was applied: $\sqrt{w}=30/F_o$, when $F_o \geq 30$ and $\sqrt{w}=1$ otherwise. The atomic scattering factors used in the calculations were taken from International Tables for X-ray Crystallography[17] and from Cromer and Mann.[18] The final atomic coordinates are listed in Table II. A list of structure factors may be obtained from the author (H.S.) on request. The difference electron density map was calculated at this stage. The sixteen hydrogen atoms bonded to N(1), N(7), N(8), N(11), N(17), N(18), N(1′), N(7′), N(8′), N(11′), N(17′), and N(18′) were clearly seen on the map and it was confirmed that the LH residues exist in keto form. No further refinement including hydrogen atoms was attempted. Calculations were carried out on HITAC 8800/8700 computers at the University of Tokyo Computer Center using X-ray System.[16]

Description of the Structure and Discussion

There are two mirror-image complex molecules (denoted as complexes A and B in Fig. 1) in a unit cell, each having two five-membered chelate rings. Unlike the six-coordinated octahedral complex of LH–Zn(II), each copper(II) complex has five coordinated bonds and assumes a distorted square pyramid structure. The ligand molecule, LH, is coordinated to the copper(II) ion through the N3 nitrogen atom of the pyrimidine ring and also through the amino nitrogen atom of the hydrazino group. The two LH residues are coordinated *trans* to each other forming a square planar coordination structure, as in the LH–Zn(II) complex. In complexes A and B, there is only one apical coordination site, occupied by the water oxygen atom.

Tables III and IV list the bond lengths and angles found in complexes A and B. The C(4)–O(9), C(14)–O(19), C(4′)–O(9′), and C(14′)–O(19′) bond lengths are 1.243, 1.245, 1.248, and 1.232 Å, respectively, suggesting the keto forms, in conformity with the IR study of LH and its complex.[5] These values of the bond length are, on the whole, appreciably shorter than corresponding the C(4)–O(9) bond length (1.264 Å) in LH–Zn(II) complex. As described before, the difference electron density map also showed that the hydrogens of the hydroxyl groups attached to C4 are transferred to the N1 atoms of the two pyrimidine rings. These nitrogen atoms form hydrogen bonds to the oxygen atoms of water, not to the chloride ions directly (the distances N(1)–H···O(1), N(11)$^{g)}$–H···O(4), N(1′)–H···O(3)$^{b)}$, and N(11′)–H···O(2) are 2.756, 2.749, 2.750, and 2.742 Å, respectively (see Table VI).

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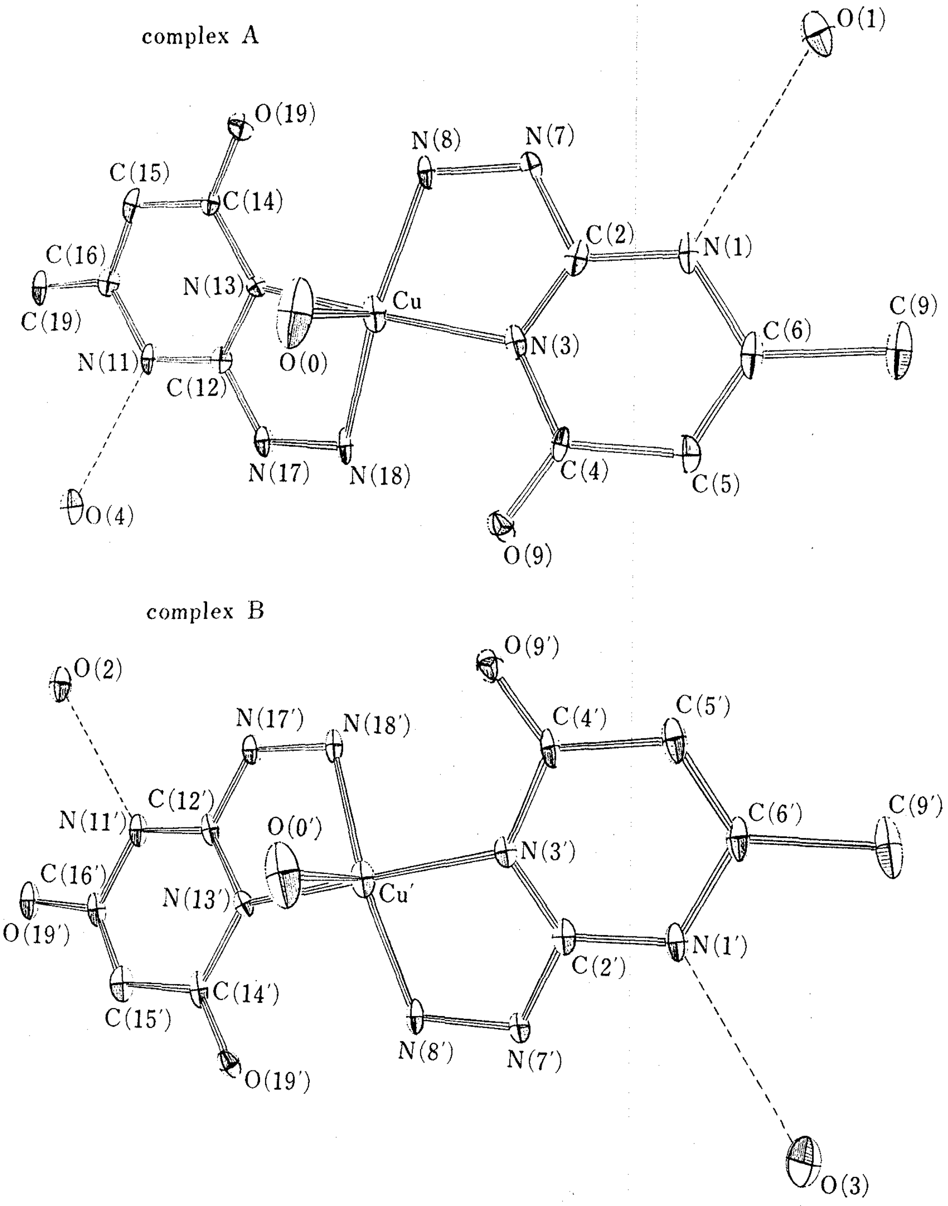

Fig. 1. Nomenclature and Perspective View of the Two Mirror-image Complex Molecules

Table III. Bond Lengths (Å) with Their Estimated Standard Deviations in Parentheses

Complex A				Complex B			
Cu— N(3)	1.981(9)	Cu— N(13)	1.983(8)	Cu′— N(3′)	1.997(9)	Cu′— N(13′)	1.986(8)
Cu— N(8)	2.038(10)	Cu— N(18)	2.015(9)	Cu′— N(8′)	1.990(9)	Cu′— N(18′)	2.033(9)
Cu— O(0)	2.208(12)			Cu′— O(0′)	2.202(12)		
N(1)-C(2)	1.333(13)	N(11)-C(12)	1.354(13)	N(1′)-C(2′)	1.343(13)	N(11′)-C(12′)	1.356(13)
N(1)-C(6)	1.399(14)	N(11)-C(16)	1.399(14)	N(1′)-C(6′)	1.393(14)	N(11′)-C(16′)	1.408(15)
C(2)-N(3)	1.303(14)	C(12)-N(13)	1.332(12)	C(2′)-N(3′)	1.280(13)	C(12′)-N(13′)	1.318(13)
C(2)-N(7)	1.373(14)	C(12)-N(17)	1.374(13)	C(2′)-N(7′)	1.373(13)	C(12′)-N(17′)	1.365(15)
N(3)-C(4)	1.395(13)	N(13)-C(14)	1.380(13)	N(3′)-C(4′)	1.416(13)	N(13′)-C(14′)	1.412(14)
C(4)-C(5)	1.454(15)	C(14)-C(15)	1.443(15)	C(4′)-C(5′)	1.439(15)	C(14′)-C(15′)	1.455(15)
C(4)-O(9)	1.243(14)	C(14)-O(19)	1.245(12)	C(4′)-O(9′)	1.248(13)	C(14′)-O(19′)	1.232(13)
C(5)-C(6)	1.354(17)	C(15)-C(16)	1.335(15)	C(5′)-C(6′)	1.350(16)	C(15′)-C(16′)	1.314(16)
C(6)-C(9)	1.494(16)	C(16)-C(19)	1.524(15)	C(6′)-C(9′)	1.527(16)	C(16′)-C(19′)	1.521(15)
N(7)-N(8)	1.431(13)	N(17)-N(18)	1.406(12)	N(7′)-N(8′)	1.430(13)	N(17′)-N(18′)	1.422(12)

Table IV. Bond Angles (°) with Their Estimated Standard Deviations in Parentheses

Complex A				Complex B			
O (0)-Cu —N (3)	93.1(4)	O (0)-Cu ——N (13)	93.1(4)	O (0′)-Cu′ —N (3′)	93.2(4)	O (0′)-Cu′ ——N (13′)	92.7(4)
O (0)-Cu —N (8)	100.3(4)	O (0)-Cu ——N (18)	101.7(4)	O (0′)-Cu′ —N (8′)	101.9(4)	O (0′)-Cu′ ——N (18′)	99.8(4)
N (3)-Cu —N (8)	81.8(4)	N (13)-Cu ——N (18)	82.3(4)	N (3′)-Cu′ —N (8′)	80.8(4)	N (13′)-Cu′ ——N (18′)	81.2(4)
N (3)-Cu —N (13)	173.6(4)	N (8)-Cu ——N (18)	158.0(4)	N (3′)-Cu′ —N (13′)	174.1(4)	N (8′)-Cu′ ——N (18′)	158.3(4)
N (3)-Cu —N (18)	97.8(4)	N (8)-Cu ——N (13)	95.8(4)	N (3′)-Cu′ —N (18′)	97.6(6)	N (8′)-Cu′ ——N (13′)	98.2(4)
C (2)-N (1)-C (6)	119.1(10)	C (12)-N (11)-C (16)	118.3(10)	C (2′)-N (1′)-C (6′)	118.3(10)	C (12′)-N (11′)-C (16′)	117.1(10)
N (3)-C (2)-N (1)	125.7(10)	N (13)-C (12)-N (11)	124.1(10)	N (3′)-C (2′)-N (1′)	125.2(10)	N (13′)-C (12′)-N (11′)	124.3(10)
N (3)-C (2)-N (7)	118.1(10)	N (13)-C (12)-N (11)	119.0(10)	N (3′)-C (2′)-N (7′)	119.2(10)	N (13′)-C (12′)-N (17′)	119.3(10)
N (1)-C (2)-N (7)	116.2(10)	N (11)-C (12)-N (17)	116.9(10)	N (1′)-C (2′)-N (7′)	115.6(10)	N (11′)-C (12′)-N (17′)	116.5(10)
C (4)-N (3)-Cu	126.2(7)	C (14)-N (13)-Cu	128.3(7)	C (4′)-N (3′)-Cu′	125.1(7)	C (14′)-N (13′)-Cu′	125.3(7)
C (4)-N (3)-C (2)	118.8(9)	C (14)-N (13)-C (12)	118.7(9)	C (4′)-N (3′)-C (2′)	120.2(9)	C (14′)-N (13′)-C (12′)	120.6(9)
Cu ——N (3)-C (2)	114.6(7)	Cu ——N (13)-C (12)	112.5(7)	Cu′ ——N (3′)-C (2′)	114.4(7)	Cu′ ——N (13′)-C (12′)	113.8(7)
C (5)-C (4)-N (3)	117.5(10)	C (15)-C (14)-N (13)	118.8(10)	C (5′)-C (4′)-N (3′)	116.1(10)	C (15′)-C (14′)-N (13′)	115.4(10)
C (5)-C (4)-O (9)	122.5(10)	C (15)-C (14)-O (19)	122.4(10)	C (5′)-C (4′)-O (9′)	123.7(10)	C (15′)-C (14′)-O (19′)	125.1(11)
N (3)-C (4)-O (9)	120.0(10)	N (13)-C (14)-O (19)	118.8(10)	N (3′)-C (4′)-O (9′)	120.2(10)	N (13′)-C (14′)-O (19′)	119.4(10)
C (6)-C (5)-C (4)	120.1(11)	C (16)-C (15)-C (14)	119.6(11)	C (6′)-C (5′)-C (4′)	120.4(11)	C (16′)-C (15′)-C (14′)	121.0(11)
C (9)-C (6)-N (1)	116.9(10)	C (19)-C (16)-N (11)	115.5(10)	C (9′)-C (6′)-N (1′)	114.7(10)	C (19′)-C (16′)-N (11′)	112.9(10)
C (9)-C (6)-C (5)	124.4(11)	C (19)-C (16)-C (15)	124.1(11)	C (9′)-C (6′)-C (5′)	125.5(11)	C (19′)-C (16′)-C (15′)	125.5(11)
N (1)-C (6)-C (5)	118.7(11)	N (11)-C (16)-C (15)	120.4(11)	N (1′)-C (6′)-C (5′)	119.8(11)	N (11′)-C (16′)-C (15′)	121.5(11)
N (8)-N (7)-C (2)	116.6(9)	N (18)-N (17)-C (12)	115.6(9)	N (8′)-N (7′)-C (2′)	113.8(9)	N (18′)-N (17′)-C (12′)	115.1(9)
Cu —N (8)-N (7)	108.7(7)	Cu ——N (18)-N (17)	110.5(7)	Cu′ ——N (8′)-N (7′)	111.6(7)	Cu′ ——N (18′)-N (17′)	110.4(7)

Table V. Deviations of Atoms from the Least-squares Planes[a)]

a) Equatorial planes about the copper atoms

$(-0.0044X - 0.0019Y + 1.0000Z = -0.2379\ \text{Å})$

N(3)	0.139	N(18)	−0.139
N(8)	−0.140	Cu	0.247*
N(13)	0.140	O(0)	2.455*

$(0.0007X + 0.0042Y + 1.0000Z = -2.0114\ \text{Å})$

N(3′)	0.138	N(18′)	−0.136
N(8′)	−0.139	Cu′	0.240*
N(13′)	0.136	O(0′)	2.443*

b) Chelate rings

$(0.0634X + 0.1656Y + 0.9841Z = -0.0053\ \text{Å})$		$(-0.0688X - 0.1648Y + 0.9839Z = -0.0089\ \text{Å})$	
Cu	0.013	Cu	0.019
C(2)	0.025	C(12)	0.026
N(3)	−0.024	N(13)	−0.029
N(7)	−0.007	N(17)	−0.001
N(8)	−0.007	N(18)	−0.015
N(1)	0.095*	N(11)	0.111*
C(4)	0.034*	C(14)	0.049*
N(13)	−0.154*	N(3)	−0.152*
N(18)	−0.723*	N(8)	−0.712*

$(0.0613X - 0.1602Y + 0.9852Z = -2.6219\ \text{Å})$		$(-0.0641X + 0.1653Y + 0.9842Z = -0.9391\ \text{Å})$	
Cu′	0.017	Cu′	0.014
C(2′)	0.022	C(12′)	0.018
N(3′)	−0.026	N(13′)	−0.021
N(7′)	0.001	N(17′)	0.000
N(8′)	−0.014	N(18′)	−0.010
N(1′)	0.084*	N(11′)	0.094*
C(4′)	0.032*	C(14′)	0.033*
N(13′)	−0.141*	N(3′)	−0.154*
N(18′)	−0.703*	N(8′)	−0.699*

c) Pyrimidine rings

$(0.0227X + 0.1610Y + 0.9867Z = -0.0913\ \text{Å})$		$(-0.0212X - 0.1647Y + 0.9861Z = -0.1090\ \text{Å})$	
N(1)	0.013	N(11)	0.019
C(2)	−0.003	C(12)	−0.002
N(3)	−0.016	N(13)	−0.021
C(4)	0.024	C(14)	0.027
C(5)	−0.015	C(15)	−0.011
C(6)	−0.003	C(16)	−0.012
Cu	0.099*	Cu	0.120*
N(7)	−0.015*	N(17)	0.000*
N(8)	0.043*	N(18)	0.054*
O(9)	0.100*	O(19)	0.096*
C(9)	−0.048*	C(19)	−0.061*

$(0.0190X - 0.1602Y + 0.9869Z = -2.9168\ \text{Å})$		$(-0.0190X + 0.1650Y + 0.9861Z = -0.8338\ \text{Å})$	
N(1′)	0.007	N(11′)	0.011
C(2′)	0.002	C(12′)	−0.005
N(3′)	−0.015	N(13′)	−0.010
C(4′)	0.018	C(14′)	0.018
C(5′)	−0.011	C(15′)	−0.013
C(6′)	−0.002	C(16′)	−0.001
Cu′	0.112*	Cu′	0.113*
N(7′)	0.007*	N(17′)	0.004*
N(8′)	0.052*	N(18′)	0.058*
O(9′)	0.092*	O(19′)	0.092*
C(9′)	−0.064*	C(19′)	−0.057*

[a)] In each of the equations for the planes, X, Y, and Z are coordinates (Å) referred to the orthogonal axes *a*, *b*, and *c*. Atoms designated by an asterisk (*) were given zero weight in calculating the planes; all other atoms were equally weighted.

Table VI. Important Intermolecular Distances of less than 3.5 Å (Å)

No.	From$^{a)}$	To	Distance	No.	From$^{a)}$	To	Distance
1	Cl(1)	O(0)$^{a)}$	3.109(11)*	21	N(18′)	O(4)$^{a)}$	2.936(13)*
2	Cl(1)	O(3)$^{a)}$	3.138(12)*	22	O(19′)	O(1)$^{a)}$	3.237(11)
3	Cl(2)	O(2)$^{a)}$	3.130(9)*	23	N(1′)	O(3)$^{b)}$	2.750(12)*
4	Cl(2)	O(4)$^{a)}$	3.177(10)*	24	N(7′)	O(19)$^{b)}$	2.732(12)*
5	Cl(3)	O(0′)$^{a)}$	3.173(13)*	25	N(8′)	O(19)$^{b)}$	3.461(12)
6	Cl(3)	O(1)$^{a)}$	3.134(11)*	26	O(1)	Cl(1)$^{b)}$	3.174(9)*
7	Cl(3)	O(3)$^{a)}$	3.180(9)*	27	Cl(2)	O(0)$^{c)}$	3.171(13)*
8	Cl(4)	O(0′)$^{a)}$	3.099(10)*	28	N(17′)	O(9)$^{c)}$	2.733(13)*
9	Cl(4)	O(4)$^{a)}$	3.153(10)*	29	N(18′)	O(9)$^{c)}$	3.450(12)
10	N(1)	O(1)$^{a)}$	2.756(12)*	30	O(2)	O(9)$^{c)}$	3.242(14)
11	N(7)	O(19′)$^{a)}$	2.749(14)*	31	O(2)	N(17)$^{c)}$	3.290(14)
12	N(7)	O(3)$^{a)}$	3.295(14)	32	O(2)	N(18)$^{c)}$	2.972(16)*
13	N(8)	O(19′)$^{a)}$	3.446(13)	33	Cl(1)	N(8)$^{d)}$	3.230(10)
14	N(8)	O(3)$^{a)}$	2.942(12)*	34	Cl(3)	N(8′)$^{d)}$	3.250(10)
15	O(19)	O(3)$^{a)}$	3.222(10)	35	Cl(4)	N(18′)$^{d)}$	3.237(13)
16	N(7′)	O(1)$^{a)}$	3.268(16)	36	Cl(4)	O(2)$^{e)}$	3.164(10)*
17	N(8′)	O(1)$^{a)}$	2.968(15)*	37	Cl(2)	N(18)$^{f)}$	3.229(12)
18	O(9′)	O(4)$^{a)}$	3.213(13)	38	O(9′)	N(17)$^{g)}$	2.722(11)*
19	N(11′)	O(2)$^{a)}$	2.742(13)*	39	O(9′)	N(18)$^{g)}$	3.427(11)
20	N(17′)	O(4)$^{a)}$	3.257(12)	40	O(4)	N(11)$^{g)}$	2.749(13)*

* Hydrogen bond suggested.

Key to the symmetry operation: *a)* x, y, z; *b)* $1+x, y, z$; *c)* $x, 1+y, z$; *d)* $x, y, 1+z$; *e)* $1+x, y, 1+z$; *f)* $x, 1+y, 1+z$; *g)* $1+x, 1+y, 1+z$.

Table VII. Distances of Intramolecular Hydrogen Bonds (Å)

No.	From	To	Distance
1	N(8)	O(19)	2.723(13)
2	O(9)	N(18)	2.745(11)
3	N(8′)	O(19′)	2.722(13)
4	O(9′)	N(18′)	2.722(11)

Table VIII. Some Relevant Interatomic Distances between the Stacked Pyrimidine Rings (Å)

From$^{a)}$	To$^{b)}$	Distance	From$^{a)}$	To$^{c)}$	Distance
N(1)	C(16)	3.507	N(1)	C(16)	3.813
N(1)	C(19)	3.657	N(1)	C(19)	3.778
C(2)	C(19)	3.590	C(2)	C(19)	3.680
C(6)	N(11)	3.821	C(6)	N(11)	3.491
C(6)	C(16)	3.762	C(6)	C(16)	3.745
C(9)	N(11)	3.793	C(9)	N(11)	3.644
C(9)	C(12)	3.708	C(9)	C(12)	3.572
N(1′)	C(16′)	3.483	N(1′)	C(16′)	3.839
N(1′)	C(19′)	3.641	N(1′)	C(19′)	3.793
C(2′)	C(19′)	3.584	C(2′)	C(19′)	3.696
C(6′)	N(11′)	3.831	C(6′)	N(11′)	3.485
C(6′)	C(16′)	3.750	C(6′)	C(16′)	3.763
C(9′)	N(11′)	3.792	C(9′)	N(11′)	3.659
C(9′)	C(12′)	3.696	C(9′)	C(12′)	3.583

a) z, y, z; *b)* $1+x, y, z$; *c)* $1+x, y, 1+z$.

The coordination bond lengths are shown in Table III. The Cu–N lengths range from 1.981 to 2.038 Å in complex A and from 1.986 to 2.033 Å in complex B. The Cu–O apical bond lengths in the A and B complexes are 2.208 and 2.202 Å, respectively.

The planarities of the equatorial planes, the chelate rings, and the pyrimidine rings are shown in Table V denoting the deviations of atoms from the least-squares planes through the planar groups. In complexes A and B, the two pyrimidine planes are inclined to each other at an angle of 18.9° (in A) and 18.8° (in B).

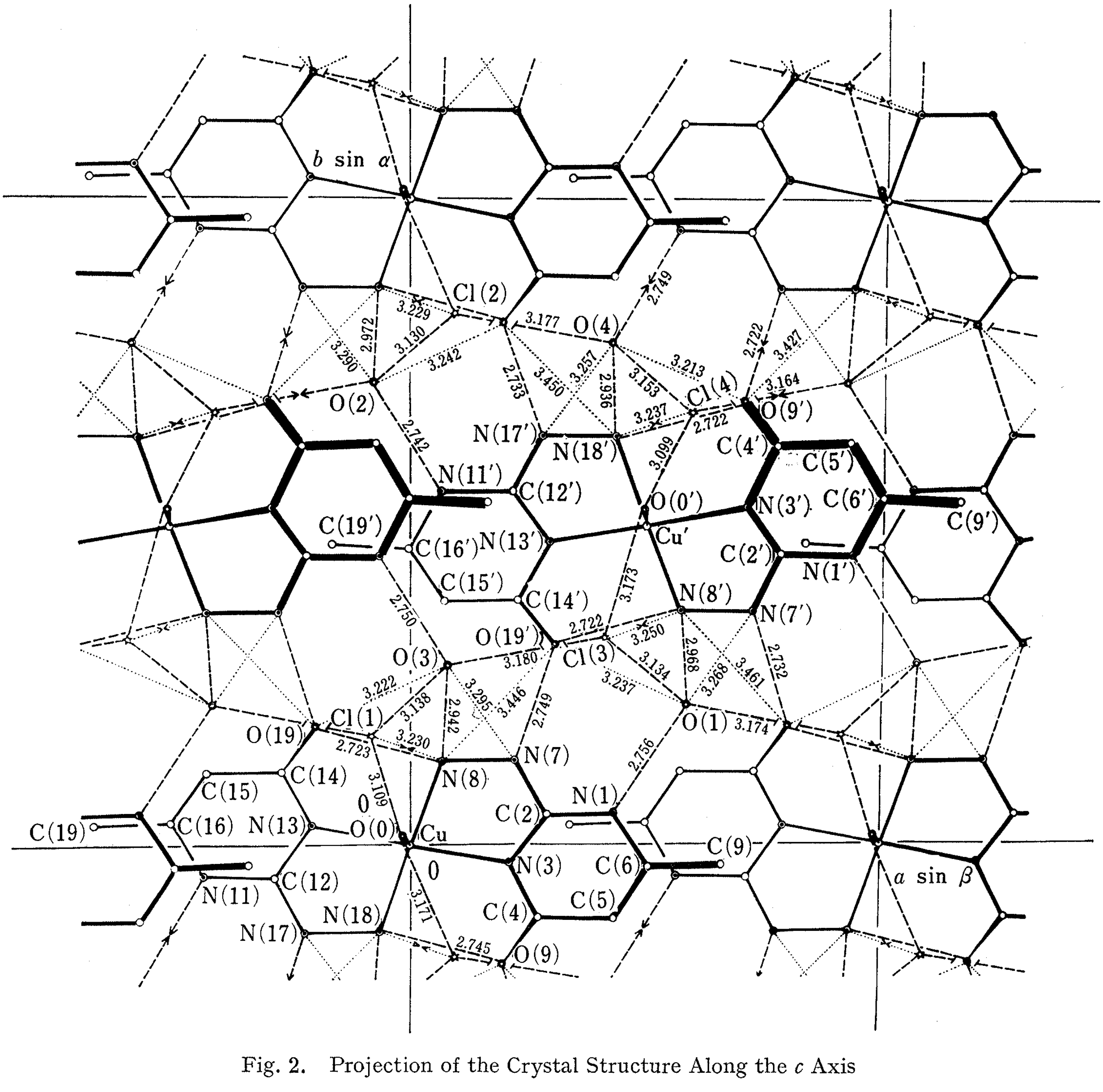

Fig. 2. Projection of the Crystal Structure Along the *c* Axis

Hydrogen bonds are shown by broken lines, and other intermolecular distances of less than 3.5 Å are shown dotted lines.

The *c* axis projection of the crystal structure is shown in Fig. 2. The complex A and B molecules are situated at the corners and centers of the unit cells in the *x*, *y* plane, linked to the neighboring complex molecules in the *b* direction mainly through hydrogen bonds. Table VI lists intermolecular interatomic distances less than 3.5 Å; hydrogen bonds are marked by an asterisk. The formation of the hydrogen bonds is suggested on the basis that the distances and directions of the bonds are reasonable and that the hydrogen atoms can be placed at reasonable positions around the donor atoms.

The hydrogen bonds connecting the complex A and B molecules are N(7)–H···O(19′), N(17)[g]–H···O(9′), N(7′)–H···O(19),[b] and N(17′)–H···O(9)[c] and the distances are 2.749, 2.722, 2.732, and 2.733 Å, respectively (see Table VI). The other hydrogen bonds are formed through water molecules or chloride ions. Besides the intermolecular hydrogen bonds shown in Table VI, there are four intramolecular hydrogen bonds listed in Table VII, which link the two ligand LH residues coordinated to the same copper(II) ion.

As shown in Fig. 2, the pyrimidine rings are stacked along the *c* axis with separation distances of about 3.4 Å. There are four kinds of stacking in the crystal structure. Some short interatomic distances between the stacked units are listed in Table VIII. It should be noted that the rings are not parallel to each other but are inclined at an angle of 18.9 or 18.8°, corresponding to the angle between the two pyrimidine rings in complex A or B, respectively.