Crystal Structures of Mixed Ligand Copper(II) Complexes Containing L-Amino Acids. I. L-Asparaginato-L-histidinato-copper(II) and Its Hydrate

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Two copper complexes containing L-histidine and L-asparagine crystallize from aqueous solution at pH 7.0. Both crystals are monoclinic, space group $P2_1$. L-Asparaginato-L-histidinatocopper(II): $a=10.913(3)$, $b=12.911(4)$, $c=10.206(3)$ Å, $\beta=113.83(2)°$, $Z=4$. L-Asparaginato-L-histidinatoaquacopper(II) trihydrate: $a=12.654(4)$, $b=11.623(4)$, $c=5.931(2)$ Å, $\beta=100.47(3)°$, $Z=2$. In both structures, four coordinating atoms in an approximately planar arrangement around copper are the α-amino and imidazole δ-nitrogen atoms of L-histidine and α-amino nitrogen and α-carboxyl oxygen of L-asparagine. The fifth coordination site is occupied by the α-carboxyl oxygen of L-histidine. Difference between the two complex crystals is found at the sixth coordination site; a water molecule is coordinated in the hydrated crystal to complete a distorted octahedral environment, while in the anhydrous crystal this site is unoccupied so that the geometry of the complex is square-pyramidal.

Studies of copper ion in normal human serum suggested that the complexes of copper and amino acids may play a part in the transport of Cu(II) between blood and tissues. Under physiological conditions, some copper complexes with mixed amino acid ligands are identified, in which histidine is primarily involved. When the second amino acid is asparagine, glutamine, or threonine, the stability of the complexes seems to be high by some cooperativity.[1,2] It is interesting to explore the coordination of these ternary complexes consisting of copper, histidine and the other amino acids at the physiological pH.

We have succeeded in preparing the single crystals of L-asparaginato-L-histidinatocopper(II) and its hydrate. The present paper deals with the structures of these two mixed ligand complexes determined by X-ray method.

Experimental

Copper hydroxide was obtained by the usual method from copper sulphate, 35% ammonia and sodium hydroxide. 1 mmol of L-asparagine (0.1311 g) and 1 mmol of L-histidine (0.1552 g), both of which were of reagent grade and purchased from Nihon Rigaku Corporation, were dissolved in 10 ml of ion-exchanged water. To this solution, 1 mmol of copper hydroxide (0.097 g) was added and the mixture was stirred for a few minutes, until intense blue colour developed. This solution was filtered to remove some copper oxide deposited in the bottom. The pH of the solution was about 7.0.

Anhydrous Crystal. Intense blue crystals with various polyhedral shapes were obtained from the filtrate by the vapor diffusion method using methanol, ethanol, or acetone. Elementary analysis. Calcd: C, 34.43; H, 4.33; N, 20.08% for $C_{10}H_{15}N_5O_5Cu$. Found: C, 34.23; H, 4.25; N, 20.04%.

Hydrated Crystal. *N,N*-Dimethylformamide was poured into the above-mentioned filtrate. Light blue single crystals were grown by standing it overnight at room temperature. The crystals were boat-shaped, the crystallographic c axis being parallel to the length of the boat. Elementary analysis. Calcd: C, 28.53; H, 5.51; N, 16.64% for $C_{10}H_{23}N_5O_9Cu$. Found: C, 28.37; H, 5.52; N, 16.58%.

Crystal Data

Anhydrous Crystal. Monoclinic, $a=10.913(3)$, $b=12.911(4)$, $c=10.206(3)$ Å, $\beta=113.83(2)°$, $D_m=1.76$ (by flotation), $D_x=1.76$ g·cm^{-3}, $Z=4$.

Hydrated Crystal. Monoclinic, $a=12.654(4)$, $b=11.623(4)$, $c=5.931(2)$ Å, $\beta=100.47(3)°$, $D_m=1.64$ (by flotation), $D_x=1.63$ g·cm^{-3}, $Z=2$.

Systematic absences for both crystals; $0k0$ for odd k. Space group $P2_1$; alternative space group $P2_1/m$ was excluded, since these crystals contain L-amino acids.

Accurate unit cell dimensions were obtained from a least-squares fit to the 2θ values measured by a diffractometer. Intensity data were collected on the Rigaku automated four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation at room temperature. A θ-2θ scan technique was employed, and reflexions for $2\theta \leqq 55°$ were recorded. A total of 2933 and 2067 non-zero reflexions out of 3154 and 2190 recorded ones were obtained for the anhydrous and hydrated crystals, respectively. Intensities were corrected for the Lorentz and polarization effects but not for absorption and secondary extinction.

Structure Determination

Anhydrous Crystal. Since Z is 4 in the space group $P2_1$, there are two molecules in an asymmetric unit. From two high peaks on the Harker section and two cross-vector peaks in general positions of the sharpened Patterson map, the coordinates of two copper atoms were deduced, the y coordinate of one copper atom being taken as 0.25. Ten light atoms around copper were located from the Fourier map phased with two copper atoms. The remaining non-hydrogen atoms were found on the next Fourier map. The structural parameters were refined by the block-diagonal least-squares method. The final R factor was 0.061 for all the reflexions and 0.049 for the non-zero reflexions.

Hydrated Crystal. The x and z coordinates of

copper were obtained from the Harker section and y was taken arbitrarily as 0.25. The Fourier map phased with the copper atom has shown a pseudo-mirror symmetry at $y=0.25$. Therefore, the positions of the nearest four atoms coordinating to the central copper atom were chosen appropriately. The other non-hydrogen atoms were obtained by successive Fourier syntheses. After the block-diagonal least-squares refinement, the final R factor was 0.093 for all the reflexions and 0.066 for the non-zero reflexions.

Atomic scattering factors were taken from "International Tables for X-Ray Crystallography."[3] The final atomic parameters are listed in Tables 1 and 2.[4]

Description of the Structure and Discussion

Crystal Structure. Figures 1 and 2 show the structures of the anhydrous and hydrated crystals, respectively, where hydrogen bonds are indicated by broken lines. Hydrogen bond lengths are listed in Table 3. In the hydrated crystal, the molecules are connected mainly through water molecules to form a three-dimensional hydrogen bond network. In the anhydrous crystal, many of the hydrogen bond lengths exceed 3 Å, suggesting that a three-dimensional

Table 1. The final fractional coordinates ($\times 10^4$) and thermal parameters ($\times 10^5$) for L-asparaginato-L-histidinatocopper(II)

Anisotropic thermal parameters are in the form: $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$.
Estimated standard deviations are in parentheses.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(A)	2363(1)	2500(1)	352(1)	427(7)	288(4)	660(8)	−97(11)	292(12)	−23(12)
Cu(B)	7510(1)	1735(1)	2594(1)	379(6)	383(5)	593(8)	63(11)	267(12)	12(13)
C(1A)	3407(8)	1184(6)	−1442(8)	752(77)	209(39)	974(93)	269(93)	492(140)	162(100)
C(2A)	2025(7)	1614(6)	−2366(7)	513(61)	378(46)	567(68)	−117(93)	79(106)	−142(98)
C(3A)	2166(7)	2640(6)	−3023(8)	726(72)	280(45)	827(83)	−56(95)	424(127)	133(99)
C(4A)	2968(7)	3442(5)	−1970(8)	689(73)	172(37)	825(84)	100(84)	268(128)	179(91)
C(5A)	3762(7)	4340(6)	−9(9)	529(69)	391(48)	994(95)	−125(96)	334(130)	−146(113)
C(6A)	3826(7)	4146(7)	−2128(8)	578(71)	434(49)	898(90)	59(100)	575(132)	289(112)
C(11A)	3216(7)	2740(5)	3290(8)	568(65)	271(43)	895(85)	55(81)	641(125)	−50(92)
C(12A)	2153(7)	1890(6)	2963(8)	519(61)	387(48)	811(78)	53(91)	618(116)	44(103)
C(13A)	2539(8)	1032(6)	4093(9)	934(88)	359(46)	975(96)	−12(109)	1124(155)	116(112)
C(14A)	3743(7)	371(6)	4215(8)	570(68)	302(41)	785(81)	−186(87)	616(124)	−131(96)
N(1A)	1227(5)	1772(6)	−1508(6)	515(52)	371(36)	794(66)	−85(86)	416(96)	−224(98)
N(2A)	2932(6)	3563(5)	−631(6)	586(59)	288(35)	708(68)	−158(75)	287(103)	−174(80)
N(3A)	4303(6)	4732(6)	−883(7)	689(66)	377(40)	1051(85)	−105(89)	647(123)	262(101)
N(11A)	1812(5)	1495(5)	1496(6)	466(52)	297(36)	717(65)	−35(68)	337(97)	0(76)
N(12A)	4310(7)	−160(6)	5431(7)	861(75)	471(47)	851(80)	−71(100)	539(127)	209(104)
O(1A)	3838(5)	1322(4)	−108(5)	714(55)	460(36)	617(56)	322(74)	122(90)	−9(74)
O(2A)	4030(7)	752(6)	−2067(7)	1094(76)	781(55)	1070(79)	944(108)	670(128)	−47(109)
O(11A)	3389(5)	3126(5)	2217(6)	713(56)	503(39)	790(62)	−289(78)	463(97)	19(82)
O(12A)	3839(6)	3032(5)	4540(6)	790(61)	677(47)	854(68)	−337(88)	469(105)	−345(94)
O(13A)	4104(5)	332(5)	3228(6)	653(54)	532(39)	907(66)	249(77)	867(100)	169(85)
C(1B)	8101(7)	2963(6)	5151(8)	589(69)	329(42)	775(82)	1(90)	468(124)	41(100)
C(2B)	6882(7)	2270(6)	4949(7)	490(60)	410(50)	623(73)	27(84)	465(110)	−78(92)
C(3B)	7283(7)	1273(6)	5826(8)	618(69)	338(42)	835(84)	51(91)	788(129)	159(100)
C(4B)	8244(7)	640(6)	5462(7)	516(64)	343(42)	606(74)	−73(87)	229(115)	−63(93)
C(5B)	9343(7)	53(6)	4238(9)	505(69)	348(45)	1091(100)	89(92)	428(136)	−103(111)
C(6B)	9097(7)	−124(6)	6231(8)	530(68)	376(47)	830(87)	1(94)	117(126)	209(107)
C(11B)	8346(7)	1550(6)	375(8)	447(61)	451(51)	863(84)	44(92)	544(120)	−53(107)
C(12B)	7098(7)	2233(7)	−297(8)	450(62)	581(58)	721(81)	−43(96)	221(116)	−216(108)
C(13B)	7331(7)	3132(7)	−1173(7)	552(70)	659(62)	540(74)	59(109)	287(119)	−78(113)
C(14B)	8443(8)	3853(7)	−289(9)	830(84)	439(51)	810(89)	−231(109)	627(143)	−81(112)
N(1B)	6140(6)	2020(5)	3416(6)	486(54)	435(42)	625(64)	77(75)	247(96)	102(82)
N(2B)	8422(6)	753(5)	4201(6)	385(51)	344(36)	765(70)	44(71)	196(98)	47(84)
N(3B)	9757(6)	−471(5)	5439(8)	648(65)	293(37)	1155(90)	151(81)	497(123)	−126(95)
N(11B)	6646(6)	2575(6)	821(7)	691(60)	504(44)	909(74)	425(101)	906(112)	29(110)
N(12B)	9356(7)	4077(6)	−805(8)	935(81)	517(49)	1300(102)	−254(109)	1161(152)	−74(121)
O(1B)	8297(6)	3139(5)	4058(6)	1098(70)	533(41)	727(62)	−702(91)	704(109)	−186(84)
O(2B)	8811(6)	3240(5)	6400(6)	791(60)	603(43)	850(66)	−352(88)	518(104)	−518(93)
O(11B)	8710(5)	1317(5)	1691(6)	598(53)	772(49)	711(61)	623(84)	334(93)	326(89)
O(12B)	8945(6)	1266(5)	−362(6)	713(58)	676(46)	963(70)	361(86)	726(106)	90(94)
O(13B)	8464(8)	4261(7)	830(7)	1556(99)	890(62)	1134(87)	−807(134)	1300(155)	−927(125)

Table 2. The final fractional coordinates ($\times 10^4$) and thermal parameters ($\times 10^5$) for L-asparaginato-L-histidinatoaquacopper(II) trihydrate

Anisotropic thermal parameters are in the form: $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$.
Estimated standard deviations are in parentheses.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	2331(1)	2500(2)	4238(2)	375(5)	239(5)	1370(22)	60(15)	586(17)	81(30)
C(1)	4106(6)	4239(9)	4509(16)	190(47)	504(70)	2387(290)	203(95)	230(184)	−134(239)
C(2)	3464(7)	4159(8)	2033(14)	380(54)	426(66)	1435(231)	−421(100)	547(182)	−519(210)
C(3)	2570(7)	5043(8)	1569(16)	527(65)	298(61)	2049(271)	122(106)	619(215)	485(216)
C(4)	1818(6)	4993(7)	3290(15)	273(49)	305(57)	1975(258)	81(89)	44(180)	−203(207)
C(5)	910(7)	4257(8)	5682(15)	385(55)	427(66)	1836(266)	223(101)	244(194)	−174(220)
C(6)	1274(7)	5871(8)	4046(17)	257(51)	407(67)	3105(337)	119(96)	327(210)	1029(250)
N(1)	3029(6)	2975(6)	1605(11)	457(48)	376(50)	1106(183)	18(86)	558(154)	−119(163)
N(2)	1607(5)	3981(6)	4308(12)	298(43)	283(49)	1783(215)	−37(77)	165(151)	−142(169)
N(3)	705(6)	5386(7)	5568(13)	318(46)	467(60)	2410(257)	65(86)	432(171)	−332(204)
O(1)	3938(5)	3452(6)	5899(11)	478(44)	613(59)	1769(192)	−74(86)	−12(149)	−41(174)
O(2)	4683(6)	5115(6)	4982(14)	423(49)	430(53)	3613(252)	6(90)	198(196)	−518(196)
C(11)	1807(7)	891(8)	7322(13)	360(53)	494(68)	1090(216)	152(100)	624(174)	−132(201)
C(12)	2233(6)	130(7)	5605(13)	320(47)	206(52)	1414(225)	48(86)	512(165)	157(178)
C(13)	2824(7)	−932(7)	6784(14)	484(58)	302(60)	1168(222)	294(98)	336(180)	38(190)
C(14)	3140(6)	−1782(7)	5094(15)	347(49)	164(50)	2200(265)	−54(84)	927(191)	−341(195)
N(11)	2879(5)	839(6)	4286(12)	295(43)	262(48)	2110(225)	52(74)	840(156)	249(168)
N(12)	3866(6)	−2570(9)	6062(11)	624(50)	298(50)	1818(190)	327(123)	686(159)	171(244)
O(11)	1827(5)	1986(5)	7031(10)	604(45)	192(37)	1444(171)	291(72)	772(141)	−87(133)
O(12)	1460(5)	445(6)	8933(11)	627(49)	408(48)	2175(204)	276(82)	1491(163)	177(164)
O(13)	2746(5)	−1792(6)	3042(10)	448(42)	556(53)	1618(184)	144(81)	2(144)	−298(165)
O(1′)	520(5)	1681(6)	1851(11)	496(44)	383(46)	2109(196)	189(74)	840(151)	23(161)
O(2′)	5524(5)	2597(9)	9093(9)	516(41)	957(71)	1481(159)	−510(123)	25(130)	662(247)
O(3′)	660(6)	−1542(7)	500(13)	611(55)	655(67)	3548(280)	−535(102)	295(197)	810(223)
O(4′)	4324(6)	805(7)	632(13)	509(47)	697(64)	2891(246)	−87(92)	574(168)	384(210)

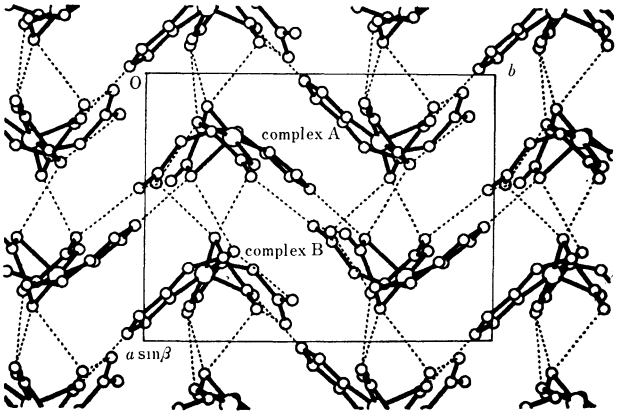

Fig. 1. Structure of the anhydrous crystal projected along c.

hydrogen bond network is not so well constructed, probably owing to the absence of water of crystallization.

Molecular Structure. The anhydrous crystal contains two crystallographically independent complexes; they are abbreviated hereafter complexes A and B, respectively. Similarly, the complex in the hydrated crystal is called as aqua complex. Figure 3 shows the stereoviews of the structures of these complexes. The bond lengths and angles are given in Fig. 4 and Table 4, respectively. Fairly good agreement among the values for corresponding bonds is observed, except for the

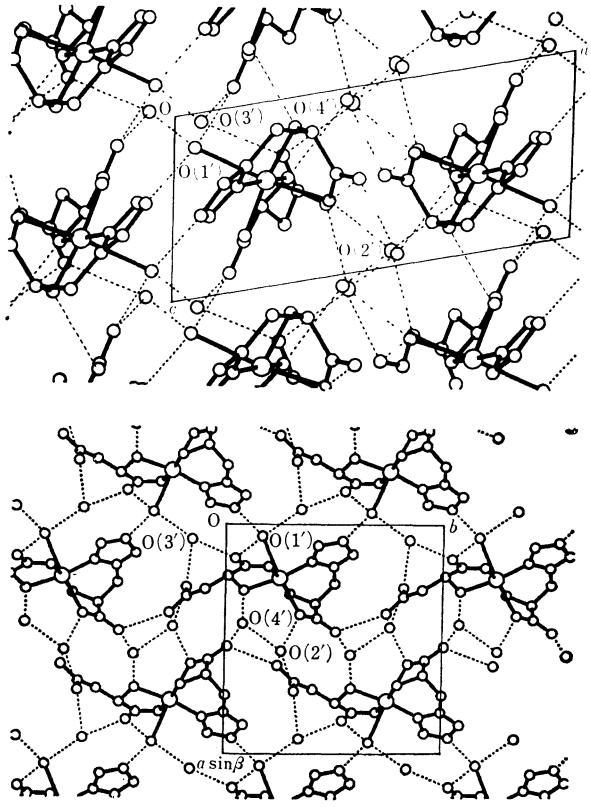

Fig. 2. Structure of the hydrated crystal projected along b (upper) and c (lower).

Table 3. Distances of hydrogen bonds(X–H···Y)

a) *Anhydrous Crystal*

X at a	Y	at	Distance X···Y (*l*/Å)
N(1A)	O(2B)	e	3.249(10)
N(1A)	O(12B)	b	3.217(10)
N(3A)	O(1A)	f	2.774(9)
N(11A)	O(13A)	a	2.840(9)
N(11A)	O(12B)	b	2.946(9)
N(12A)	O(2A)	c	2.937(11)
N(12A)	O(12A)	g	3.079(10)
N(1B)	O(11A)	a	3.095(9)
N(3B)	O(13A)	a	3.062(9)
N(3B)	O(1B)	h	2.667(10)
N(11B)	O(13B)	a	2.943(11)
N(11B)	O(1A)	a	3.250(10)
N(12B)	O(2B)	d	2.879(11)

Code of symmetry related position

a: x, y, z
b: $-1+x, y, z$
c: $x, y, 1+z$
d: $x, y, -1+z$
e: $-1+x, y, -1+z$
f: $1-x, 0.5+y, -z$
g: $1-x, -0.5+y, 1-z$
h: $2-x, -0.5+y, 1-z$

b) *Hydrated Crystal*

X at a	Y	at	Distance X···Y (*l*/Å)
O(1′)	O(3′)	d	2.772(10)
O(1′)	O(12)	c	2.687(9)
O(2′)	O(1)	a	2.688(13)
O(2′)	O(13)	f	2.812(13)
O(3′)	O(12)	c	2.750(10)
O(3′)	O(13)	a	2.807(11)
O(4′)	O(2)	g	2.792(11)
O(4′)	O(2′)	c	2.825(13)
N(1)	O(11)	c	3.081(10)
N(3)	O(1′)	e	2.806(10)
N(11)	O(4′)	a	3.080(11)
N(12)	O(2′)	h	2.844(15)
N(12)	O(2)	b	2.993(13)

Code of symmetry related position

a: x, y, z
b: $x, -1+y, z$
c: $x, y, -1+z$
d: $-x, 0.5+y, -z$
e: $-x, 0.5+y, 1-z$
f: $1-x, 0.5+y, 1-z$
g: $1-x, -0.5+y, 1-z$
h: $1-x, -0.5+y, 2-z$

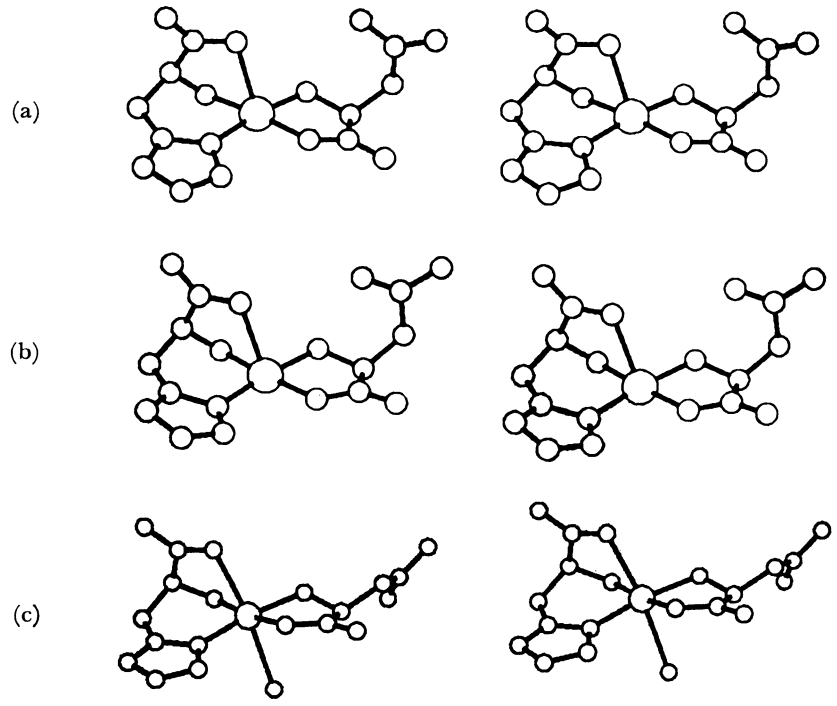

Fig. 3. Stereoviews of the structures of complex A (a), complex B (b), aqua complex (c).

values relating to the metal chelation.

For three kinds of complexes in common, L-asparagine molecule coordinates to copper through the α-amino nitrogen and α-carboxyl oxygen, and L-histidine through the α-amino nitrogen, imidazole δ-nitrogen, and α-carboxyl oxygen. These atoms except the last one occupy the corners of the planar coordination square. The coordination distances, especially for Cu–N(2) and Cu–N(11), vary significantly among three kinds of complexes (the maximum difference is 0.058 Å). But

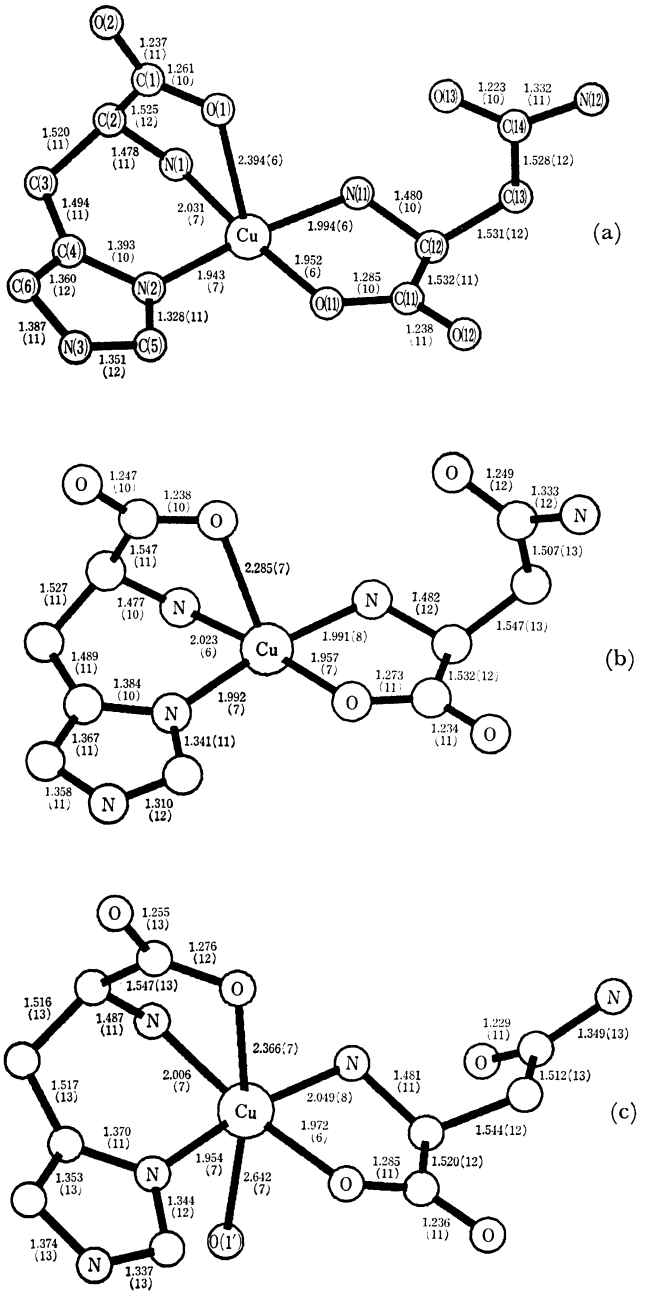

Fig. 4. Bond lengths (l/Å) in complex A (a), complex B (b), and aqua complex (c).
Estimated standard deviations in the last digits are in parentheses.

there are no correlation between the distances and any other geometrical features. The α-carboxyl oxygen atom in L-histidine deviates from the normal axial position, the angle N(1)–Cu–O(1) being 74.2, 74.3, and 74.3° for A, B, and aqua complexes, respectively. Such deviations may be due to the constraint of the histidine molecule. Axial bond length in complex B, 2.285 Å, is the shortest among the copper complexes containing amino acids or peptides.[5] The coordination geometry of these three complexes is the same as that of L-histidinato-L-threoninatoaquacopper(II) hydrate reported by Freeman *et al.*[6] Since the N(1)–Cu–O(1) angle in this complex is 68.3°, overlapping between d_{z^2} of copper and

Table 4. Bond angles (θ/°)

	Complex A	Complex B
a) *Anhydrous Crystal*		
O(1)–Cu–O(13)	106.7(2)	112.4(3)
O(1)–Cu–N(1)	74.2(3)	74.3(3)
O(1)–Cu–N(2)	88.1(2)	92.0(3)
O(1)–Cu–N(11)	95.0(2)	94.4(3)
N(1)–Cu–N(2)	92.7(3)	88.9(3)
N(1)–Cu–N(11)	91.8(3)	96.9(3)
N(1)–Cu–O(11)	175.3(3)	173.3(3)
N(2)–Cu–O(11)	91.9(3)	90.4(3)
N(2)–Cu–N(11)	175.1(3)	172.3(3)
O(11)–Cu–N(11)	83.6(3)	83.3(3)
O(1)–C(1)–O(2)	125.3(8)	127.3(8)
O(1)–C(1)–C(2)	117.4(7)	116.0(7)
O(2)–C(1)–C(2)	117.3(8)	116.6(7)
C(1)–C(2)–C(3)	109.9(8)	112.4(6)
C(1)–C(2)–N(1)	110.9(7)	110.0(6)
N(1)–C(2)–C(3)	109.3(7)	110.0(6)
C(2)–C(3)–C(4)	114.9(7)	112.4(7)
C(3)–C(4)–C(6)	127.6(8)	129.7(7)
C(3)–C(4)–N(2)	122.9(7)	123.5(7)
N(2)–C(4)–C(6)	109.6(7)	106.9(7)
N(3)–C(5)–N(2)	111.3(8)	110.2(8)
C(4)–C(6)–N(3)	106.2(7)	107.4(7)
C(5)–N(3)–C(5)	107.3(7)	108.7(8)
C(4)–N(2)–C(5)	105.6(7)	106.8(7)
C(4)–N(2)–Cu	124.7(5)	128.4(5)
C(5)–N(2)–Cu	125.8(6)	124.8(6)
C(2)–N(1)–Cu	109.5(5)	107.4(5)
O(11)–C(11)–O(12)	123.4(8)	123.8(8)
O(11)–C(11)–C(12)	116.9(7)	116.7(7)
O(12)–C(11)–C(12)	119.7(7)	119.5(7)
C(11)–C(12)–N(11)	109.0(6)	109.8(7)
C(11)–C(12)–C(13)	113.6(7)	111.5(7)
N(11)–C(12)–C(13)	113.1(6)	113.9(7)
C(12)–C(13)–C(14)	115.6(7)	113.5(8)
C(13)–C(14)–O(13)	120.6(7)	121.4(9)
C(13)–C(14)–N(12)	115.1(7)	116.6(8)
O(13)–C(14)–N(12)	124.3(8)	121.9(9)
C(11)–O(11)–Cu	116.5(5)	116.7(6)
C(12)–N(11)–Cu	110.9(5)	110.8(6)

b) *Hydrated Crystal*

O(1)–Cu–N(1)	74.3(3)	O(2)–C(1)–C(2)	116.4(9)
O(1)–Cu–N(2)	87.1(3)	C(1)–C(2)–C(3)	112.2(8)
O(1)–Cu–N(11)	99.9(3)	C(1)–C(2)–N(1)	109.4(7)
O(1)–Cu–O(11)	100.2(3)	N(1)–C(2)–C(3)	110.8(7)
O(1)–Cu–O(1′)	170.8(2)	C(2)–C(3)–C(4)	113.0(8)
O(1′)–Cu–N(1)	98.3(3)	C(3)–C(4)–C(6)	127.8(8)
O(1′)–Cu–N(2)	88.0(3)	C(3)–C(4)–N(2)	121.7(8)
O(1′)–Cu–N(11)	85.8(3)	N(2)–C(4)–C(6)	110.5(8)
O(1′)–Cu–O(11)	87.7(2)	N(3)–C(5)–N(2)	110.2(8)
N(1)–Cu–N(2)	92.8(3)	C(4)–C(6)–N(3)	105.5(9)
N(1)–Cu–N(11)	94.3(3)	C(5)–N(3)–C(6)	108.4(8)
N(1)–Cu–O(11)	172.9(3)	C(4)–N(2)–C(5)	105.4(7)
N(2)–Cu–O(11)	91.4(3)	C(4)–N(2)–Cu	128.1(6)
N(2)–Cu–N(11)	171.2(3)	C(5)–N(2)–Cu	125.8(6)
O(11)–Cu–N(11)	82.2(3)	C(2)–N(1)–Cu	108.9(5)
O(1)–C(1)–O(2)	126.6(9)	O(11)–C(11)–O(12)	122.6(8)
O(1)–C(1)–C(2)	116.7(8)	O(11)–C(11)–C(12)	117.9(8)
O(12)–C(11)–C(12)	119.5(8)	C(13)–C(14)–N(12)	113.8(8)
C(11)–C(12)–C(13)	111.3(7)	C(13)–C(14)–O(13)	123.6(8)
C(11)–C(12)–N(11)	109.1(7)	O(13)–C(14)–N(12)	122.6(9)
N(11)–C(12)–C(13)	114.6(7)	C(11)–O(11)–Cu	115.5(6)
C(12)–C(13)–C(14)	112.8(7)	C(12)–N(11)–Cu	108.3(5)

lone-pair orbital of oxygen is less, so that the Cu–O (axial) length (2.58 Å) is longer than the values in the present three complexes.

In the hydrated crystal, the copper coordination is octahedral; water molecule occupies the sixth coordination site at a distance of 2.642 Å. It is noted that this also occurs in rather oblique direction, O(water)–Cu–O(11) being 87.7°, perhaps owing to the trans effect. The atoms forming the coordination square are not precisely coplanar. Their deviations may be described as a very flattened tetrahedron. The dihedral angle between the two planes, N(1)–Cu–N(2) and N(11)–Cu–O(11), is 8.5(3)°. Such deformation from the square planar coordination is attributed to the geometrical constraint owing to the chelation of L-histidine as a tridentate ligand, since bishistaminocopper(II) perchlorate[7] has exactly and bis(L-asparaginato)copper(II)[8] has almost square-planar coordination.

In the anhydrous crystal, the copper atom is five-coordinated, forming a square pyramid. The copper atoms in A and B complexes are out of the best plane for the equatorial coordinating atoms toward the top of the pyramid (0.023 and 0.099 Å, respectively). This is because of the disproportion of the charge, and is the general trend for the square-pyramidal environment of copper complexes. The sixth sites are blocked by carbonyl oxygen O(12B) and amino nitrogen N(12B) for complex A and imidazole nitrogen N(3A) for complex B. The distances from these atoms to copper are 3.846(7), 3.631(9), and 3.295(7) Å, respectively.

The imidazole rings in these complexes are planar within the experimental errors. The ring planes make dihedral angles of 19.9(3), 11.5(3), and 13.1(3)° with the copper square planes for A, B, and aqua complexes, respectively.

Side chains of asparagine in anhydrous complexes have a compact form puckered onto the coordination square, as shown in Fig. 3, while that in aqua complex has an extended one. As for the conformation around C(12)–C(13), C(14) is gauche to C(11) and N(11) in the former, and C(14) is trans to C(11) in the latter. The conformation of the former may be stabilized by the intramolecular hydrogen bond O(13)···N(11) in both of A and B complexes.

For mixed ligand copper(II) complexes involving an acidic amino acid and a basic amino acid, the electrostatic ligand-ligand interaction between their charged side chains has been proposed on the basis of the synthetic and CD spectral studies.[9,10] Also, successful optical resolution of DL-histidine *via* formation of the ternary complex with L-asparagine has been inferred to be due to the intramolecular hydrogen bonding between the polar side chains[11] in solution. Although such ligand-ligand interactions have not been realized in the structures of the present three complexes, they may occur under favourable conditions by the conformational change around C(12)–C(13) and C(13)–C(14) of asparagine, and the present study has revealed that the conformation around these bonds is flexible for the change of crystalline environment.

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