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Structure of Aquachloro(4-hydroxy-L-prolinato)copper(II)

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An X-ray diffraction study of the title complex has been carried out. The crystal is monoclinic, with the space group $P2_1$; Z=2, a=8.712(1), b=6.055(1), c=8.187(1) Å, β=109.83(1)°. Block-diagonal least-squares refinements have led to the final R value of 0.052. The structure consists of a one-dimensional polymer chain bridged by only one carboxylato group of a 4-hydroxy-L-prolinato ligand. The chains are parallel to the b axis; each is connected with the neighboring one by hydrogen bonds between water oxygen atoms and chlorine atoms. Thus a sheet forms parallel to the (0 0 1) plane. One carboxylato oxygen atom of the 4-hydroxy-L-prolinato ligand is coordinated to two copper atoms, and the other is coordinated to one of these two copper atoms. The copper atom is surrounded by three carboxylato oxygen atoms, one water oxygen atom, one nitrogen atom in a pyrrolidine ring, and one chlorine atom. Therefore the copper atom has distorted octahedral coordination.

The amino acids having a pyrrolidine ring, 4-hydroxy-L-proline (Hhpro) and L-proline (Hpro), are a little different from other α-amino acids. Some interesting properties of their metal complexes have been reported: for example, the studies of circular dichroism spectra[1,2] and of stereoisomerism.[3] The properties of their complexes are based on the structures. Therefore studies about syntheses, properties, and structures of some metal complexes with Hhpro and Hpro have been carried out in our group.[4—6]

Two copper(II) complexes with hpro has been reported:[5] one is [Cu(hpro)$_2$] and the other is [CuCl(hpro)(H$_2$O)]. The structure of the latter complex was determined by infrared spectra. In the free ligand, Hhpro, there are some peaks assigned to NH_2^+ stretching and bending vibrations. On the other hand, in the complex there are peaks assigned to NH vibrations without any assigned to NH_2^+. The peak assigned to Cu-Cl stretching vibration is observed at about 280 cm^{-1}. This is a rather low frequency, if we assume that the chlorine atom is a terminal one. For example, ν_{CuX}(terminal)=311 cm^{-1}, ν_{CuX}(bridge)=280, 230 cm^{-1} for $(NH_4)_2[Cu_2Cl_6]$, ν_{CuX}(terminal)=301 cm^{-1}, ν_{CuX}(bridge)=278, 236 cm^{-1} for $K_2[Cu_2Cl_6]$.[7] Therefore the peak should be considered to be based on the bridged chlorine atom and the metal bonding. However, it is difficult to determine the structure from the infrared spectra.

In this work, the confirmation of the structure [CuCl(hpro)(H$_2$O)] by an X-ray diffraction study and the interpretation of the properties based on the structure were carried out.

Experimental

Preparation of the Sample. The samples for the X-ray diffraction study were prepared in the following way, modifying the previous method:[5] equimolar amounts of $CuCl_2 \cdot 2H_2O$ and Hhpro were mixed in aqueous solution, then the aqueous solution was condensed at 60—70 °C for several hours. The sample crystals were obtained from the aqueous solution of the complex by keeping it in a desiccator containing acetone for several days.

Table 1. Crystal Data

$CuCl(C_5H_8NO_3)(H_2O)$	$F.W.$ = 247.14
Monoclinic	Space group $P2_1$
a = 8.712(1) Å	
b = 6.055(1) Å	β = 109.83(1)°
c = 8.187(1) Å	
Z = 2	U = 406.3(1) Å^3
D_m = 2.015(3) g cm^{-3}	D_x = 2.020 g cm^{-3}
μ(Mo $K\alpha$) = 30.9 cm^{-1}	

X-Ray Measurements and Structure Determination. The crystal data are given in Table 1. The reflection intensities were collected by the θ—2θ scan techniqe ($2\theta<76°$) on a Philips PW1100 automated four-circle diffractometer. The 2253 intensities ($|F_o|>3\sigma(|F_o|)$) were corrected for Lorentz and polarization factors, but not for absorption, because of the low magnitude of μr(=0.46). All calculations were carried out on a HITAC M-200H/M-280H computer at the Computer Center of The University of Tokyo, using the local version of the UNICS.[8] The scattering factors were taken from tables.[9] The structure was solved by a heavy-atom method and refined by a block-diagonal least-squares method. The positions of hydrogen atoms, except for hydroxyl and water hydrogen atoms, were obtained by difference-Fourier syntheses. The weighting scheme was $W=1/[\{\sigma(|F_o|)\}^2+(0.02\times|F_o|)^2]$. The final R value[10] was 0.052.

Results and Discussion

The final atomic parameters are listed in Table 2,[11] the interatomic distances in Table 3, and the bond angles in Table 4. The perspective drawing of the complex and the numbering scheme of the atoms are shown in Fig. 1.

The structure of the complex consists of a one-dimensional polymer chain bridged by only one carboxylato group of hpro. One carboxylato oxygen atom of the hpro is coordinated to two copper atoms to form an oxygen bridge, and the other is coordinated to one of these two copper atoms.

The copper atom is surrounded by six atoms: Three carboxylato oxygen atoms, one water oxygen atom, one nitrogen atom in a pyrrolidine ring, and one chlorine atom. Among them, the O(11)$^{\rm I}$ and Cl are at a longer distance from the metal than the others. The angle O(11)$^{\rm I}$-Cu-O(12)$^{\rm I}$ is 54.4(1)°. Therefore the octahedron surrounding the copper atom is extremely distorted.

The prediction given by the infrared spectra was confirmed: The nitrogen atom in the pyrrolidine ring

Table 2. Final Positional Parameters ($\times 10^4$ for non-hydrogen atoms; $\times 10^3$ for hydrogen atoms) and equivalent isotropic temperature factors ($B_{\rm eq}$/Å^2),[a] with the estimated standard deviations.

Atom	X	Y	Z	$B_{\rm eq}$/Å^2
Cu	1873.1(4)	−2500	4807.6(4)	1.42
Cl	3041(1)	−5540(2)	3373(2)	2.45
O(11)	331(3)	−4442(5)	5303(3)	1.87
O(12)	−158(3)	−6389(5)	7344(3)	1.79
O(4)	4170(3)	−1044(6)	11145(3)	2.17
O(W)	3417(3)	−391(5)	4353(4)	2.09
N	3045(3)	−2551(6)	7406(3)	1.41
C(1)	661(4)	−4987(5)	6882(4)	1.35
C(2)	2052(4)	−3832(5)	8241(4)	1.36
C(3)	1430(4)	−2140(7)	9258(5)	2.18
C(4)	2750(4)	−377(6)	9737(4)	1.88
C(5)	3227(5)	−247(7)	8119(4)	2.14
				$B_{\rm iso}$/Å^2
H(2)[b]	268(5)	−502(10)	904(7)	1.2(8)
H(31)	153(7)	−284(14)	1000(9)	3.6(15)
H(32)	55(8)	−180(19)	852(14)	5.2(20)
H(4)	229(6)	103(12)	991(8)	1.8(10)
H(51)	247(6)	56(11)	725(9)	2.4(12)
H(52)	477(10)	−55(28)	837(16)	8.6(31)
H(N)	390(5)	−330(10)	775(7)	1.2(9)

a) The equivalent isotropic temperature factors for non-hydrogen atoms were computed using the following expression:

$$B_{\rm eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{13}ac\cos\beta).$$

The B_{ij}'s are in the form:

$$\exp\{-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2klB_{23}+2hlB_{13}+2hkB_{12})\}.$$

b) The numbering scheme of hydrogen atoms is based on the number of the atom attached to the hydrogen atoms.

Table 3. Interatomic Distances (l/Å), with the Estimated Standard Deviations in Parentheses

Cu-Cl	2.571(2)	C(1)-C(2)	1.510(5)
Cu-O(11)	1.930(4)	C(2)-C(3)	1.530(7)
Cu-O(11)$^{\rm I}$	2.647(4)	C(3)-C(4)	1.519(5)
Cu-O(12)$^{\rm I}$	2.001(3)	C(4)-C(5)	1.519(9)
Cu-O(W)	1.980(4)	C(4)-O(4)	1.434(5)
Cu-N	2.024(5)	C(5)-N	1.499(6)
C(1)-O(11)	1.269(7)	N-C(2)	1.490(6)
C(1)-O(12)	1.248(5)		
C(2)-H(2)	1.00(7)	C(5)-H(51)	0.93(8)
C(3)-H(31)	0.73(12)	C(5)-H(52)	1.34(10)
C(3)-H(32)	0.83(10)	N-H(N)	0.84(5)
C(4)-H(4)	0.98(8)		
O(W)-Cl$^{\rm II}$	3.034(5)	Cl-O(W)$^{\rm III}$	3.017(3)

Key to symmetry operations: I. $-x$, $0.5+y$, $1.0-z$; II. x, $1+y$, z; III. $1-x$, $-0.5+y$, $1-z$.

Table 4. Bond Angles (ϕ/°), with the Estimated Standard Deviations in Parentheses

Cl-Cu-O(11)	94.1(1)	C(1)$^{\rm I}$-O(11)$^{\rm I}$-Cu	76.4(3)
Cl-Cu-O(W)	88.7(1)	C(1)$^{\rm I}$-O(12)$^{\rm I}$-Cu	107.2(3)
Cl-Cu-N	109.4(2)	O(11)-C(1)-O(12)	122.1(4)
Cl-Cu-O(11)$^{\rm I}$	151.6(1)	O(11)-C(1)-C(2)	118.5(4)
Cl-Cu-O(12)$^{\rm I}$	97.6(1)	O(12)-C(1)-C(2)	119.3(4)
O(11)-Cu-O(W)	177.3(2)	C(1)-C(2)-N	110.4(4)
O(11)-Cu-N	84.7(2)	C(1)-C(2)-C(3)	111.5(3)
O(11)-Cu-O(11)$^{\rm I}$	83.4(1)	N-C(2)-C(3)	105.6(3)
O(11)-Cu-O(12)$^{\rm I}$	91.5(1)	C(2)-C(3)-C(4)	103.5(4)
O(W)-Cu-N	94.4(2)	C(3)-C(4)-O(4)	112.3(4)
O(W)-Cu-O(11)$^{\rm I}$	94.2(1)	O(4)-C(4)-C(5)	107.5(4)
O(W)-Cu-O(12)$^{\rm I}$	88.2(1)	C(3)-C(4)-C(5)	102.6(4)
N-Cu-O(11)$^{\rm I}$	98.6(2)	C(4)-C(5)-N	105.5(4)
N-Cu-O(12)$^{\rm I}$	153.0(2)	Cu-N-C(5)	110.1(3)
O(11)$^{\rm I}$-Cu-O(12)$^{\rm I}$	54.4(1)	Cu-N-C(2)	109.1(2)
Cu-O(11)-C(1)	116.1(3)	C(5)-N-C(2)	107.9(4)
Cu-O(11)$^{\rm I}$-Cu$^{\rm I}$	165.5(2)		

Key to symmetry operation: I. $-x$, $0.5+y$, $1.0-z$.

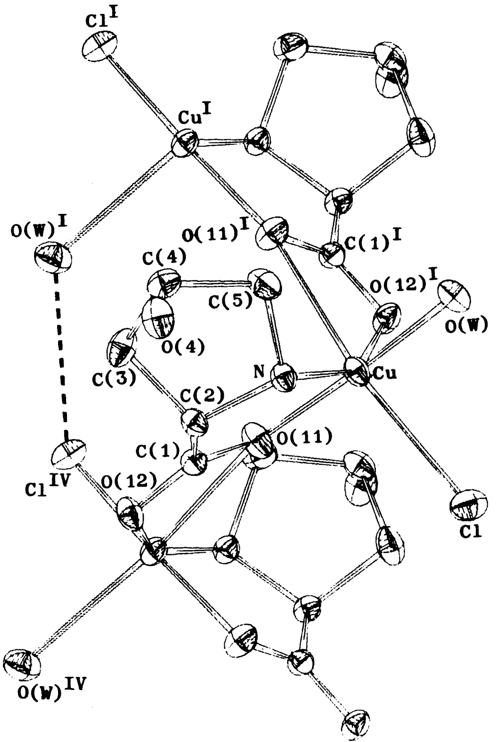

Fig. 1. The perspective drawing of [CuCl(hpro)(H_2O)] and the numbering scheme of the atoms. (----: Hydrogen bonding).

Key to symmetry operations: I. $-x$, $0.5+y$, $1.0-z$; IV. $-x$, $-0.5+y$, $-z$.

is coordinated to the metal. The bond length of Cu-N, 2.024(5) Å, is not very different from that of common amino acid chelate compounds.

The distance of Cu-O(11)$^{\mathrm{I}}$, 2.647(4) Å, is rather longer than the common Cu-O bond. However, this is not so surprising, because similar or more extreme examples have been reported in copper(II) oxalate,$^{12)}$ bis[(alkylthio)acetato]copper(II)-amine adduct,$^{13)}$ and mixed amino acid copper complexes.$^{14,15)}$ The chlorine atom is coordinated to the metal not as a bridging atom, but as a terminal one. In the classification according to bond lengths, the Cu-Cl bond, 2.571(2) Å, however, should belong to Cu-Cl(bridging) rather than of Cu-Cl(terminal). For example, Cu-Cl(bridging): 2.337 Å and 2.769 Å in dichloro(1,2,4-triazole)copper(II),$^{16)}$ Cu-Cl(terminal): 2.241(6) Å in dichlorobis(tetramethylthiourea)copper(II).$^{17)}$

The bond distances and angles of the binding hpro are not very different from those of the free molecule. In the free molecule the four atoms of a pyrrolidine ring are nearly coplanar, except for the carbon atom carrying a hydroxyl group.$^{18)}$ On coordination, however, the pyrrolidine ring is bent on the line from N to C(3), and C(4) and C(5) deviate from the plane formed by C(2), N, and C(3) in the direction against the carboxylato group. The deviation is in the opposite direction to that of the Hhpro in [CdCl$_2$(Hhpro)].$^{4)}$

There are two types of chelate rings in this complex. One is the five-membered ring which is formed by Cu, O(11), C(1), C(2), and N, the other is the four-membered ring formed by Cu, O(11)$^{\mathrm{I}}$, C(1)$^{\mathrm{I}}$, and O(12)$^{\mathrm{I}}$. Both chelate rings are fairly flat planes, as shown in Table 5. They neighbor each other between two copper atoms. The dihedral angle of these chelate rings is 172.5°.

Table 5. Least-Squares Planes and the Deviations of Atoms (l/Å)

Plane (1) [Cl, O(11), O(W), O(11)$^{\mathrm{I}}$]
$-0.2465X+0.05472Y-0.9676Z-3.4549=0$
Cl, 0.3355; O(11), −0.3524; O(W), −0.2376;
O(11)$^{\mathrm{I}}$, 0.3657; Cu, −0.2839

Plane (2) [O(11), O(W), N, O(12)$^{\mathrm{I}}$]
$0.5469X-0.7554Y-0.3608Z-0.3007=0$
O(11), 0.2149; O(W), 0.2397; N, −0.2594;
O(12)$^{\mathrm{I}}$, −0.1281; Cu, 0.2739

Plane (3) [Cl, N, O(11)$^{\mathrm{I}}$, O(12)$^{\mathrm{I}}$]
$0.7260X+0.6777Y-0.1165Z-1.3053=0$
Cl, −0.0299; N, 0.0218; O(11)$^{\mathrm{I}}$, −0.0467;
O(12)$^{\mathrm{I}}$, 0.0596; Cu, 0.603

Plane (4) [Cu, O(11), C(1), C(2), N]
$-0.6098X+0.7897Y+0.0676Z-1.1583=0$
Cu, 0.0286; O(11), 0.0285; C(1), −0.0589;
C(2), 0.0545; N, −0.0449

Plane (5) [Cu, O(12)$^{\mathrm{I}}$, C(1)$^{\mathrm{I}}$, O(11)$^{\mathrm{I}}$]
Cu, −0.0030; O(12)$^{\mathrm{I}}$, 0.0073; C(1)$^{\mathrm{I}}$, −0.0093;
O(11)$^{\mathrm{I}}$, 0.0051

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} a & b\cos\gamma & c\cos\beta \\ 0 & b\sin\gamma & -c\cos\alpha^{*}\sin\beta \\ 0 & 0 & c\cos\alpha^{*}\sin\beta \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Key to symmetry operation: I. $-x$, $0.5+y$, $1.0-z$.

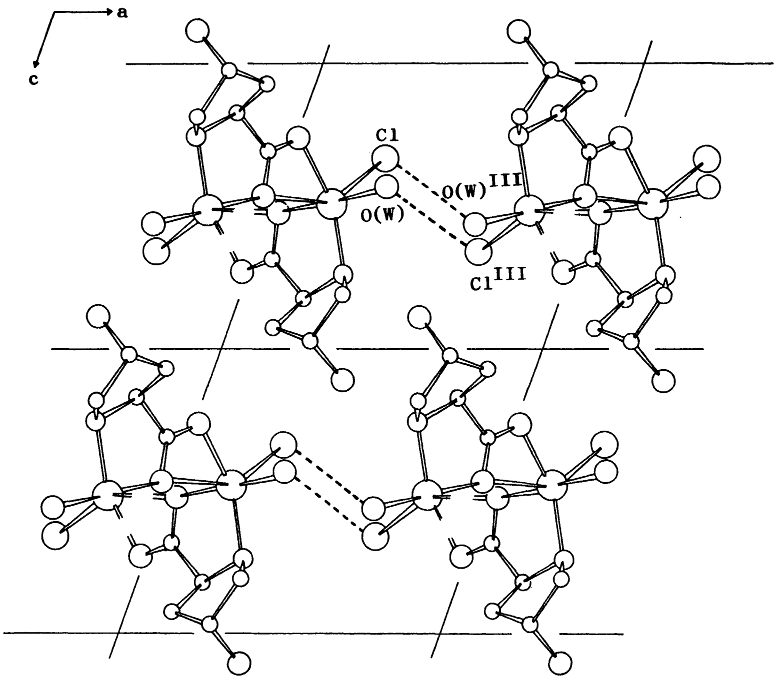

Fig. 2. The projection of the structure along the b axis. (----: Hydrogen bonding). Key to symmetry operation: III. $1.0-x$, $-0.5+y$, $1.0-z$.

The projection of the structure along the b axis is given in Fig. 2. There are two types of hydrogen bonds between the water oxygen and the chlorine atoms. One is the intra-chain hydrogen bond (O(W)-Cl^{II}=3.034(5) Å), shown with broken line, between O(W)^{I} and Cl^{IV}, in Fig. 1. The other is the inter-chain hydrogen bond (Cl-O(W)^{III}=3.017(3) Å; see Fig. 2). The rather long bond length of Cu-Cl may be due to the intra- and inter-chain hydrogen bonds. Each chain arranged in parallel with the b axis is linked to the neighboring one, by hydrogen bonds. Thus, a sheet forms parallel to the (001) plane, as shown in Fig. 2. The oxygen atom of the hydroxyl group does not form any hydrogen bonds. On the basis of the structural data, the properties of the complex reported previously[5] are reconsidered.

In the infrared spectra, the peak assigned to Cu-Cl stretching vibration, about 280 cm^{-1}, is a rather low frequency for Cu-Cl(terminal) bonding. In the complex, [CuCl(hpro)(H_2O)], the peaks of carboxylato group stretching vibrations are at 1592 and 1567 cm^{-1} (COO$^-$ antisymmetric) and at 1407 and 1393 cm^{-1} (COO$^-$ symmetric). In the bis-chelate complex, [Cu(hpro)$_2$], the peaks are at 1592 cm^{-1} (COO$^-$ antisymmetric) and 1407 cm^{-1} (COO$^-$ symmetric).[5] The splitting peaks of antisymmetric and symmetric stretching vibrations in the former complex may result from the complicated bridging carboxyl group as mentioned above. The difference between the mean value of COO$^-$ antisymmetric vibrations and that of COO$^-$ symmetric vibrations in [CuCl(hpro)(H_2O)] is smaller than the difference between two peaks of antisymmetric and symmetric vibrations in [Cu(hpro)$_2$] or in free ligand (Hhpro). This fact agrees with the vibrational spectrum patterns of behavior established for the carboxylato ligand:[19,20] in the bidentate (chelate) carboxylato complex, the separation between the COO$^-$ stretching vibrations is smaller than that of the free carboxylate ion or of the unidentate carboxyl complex.

The electronic spectrum of the aqueous solution is different from the powder diffuse reflection one in [CuCl(hpro)(H_2O)]. This indicates that the complex has different coordination types in the aqueous solution and in the crystalline form. In the aqueous solution there is a broad peak at 680 nm, which is characteristic of a six-coordinated Cu^{II} complex. On the other hand, the peak at 769 nm has a shoulder near 900 nm in the powder diffuse reflection:[21] This may result from some extreme distortion of the octahedron surrounding copper(II). This result suggests that the coordination polyhedron changes from its distorted shape into a shape nearer an octahedron, because the polymer chain cleaves and then an octahedron is rebuilt by becoming coordinated to water molecules in the aqueous solution.

The magnetic or thermal properties of this complex are consistent with the structure proposed.

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21) The data in Ref. 5 was measured by a Hitachi 624 digital spectrophotometer (190—900 nm). In this work, the data obtained by means of a JASCO UVIDEC-590 NIR spectrophotometer (700—2500 nm) were added. From the data, the shoulder near 900 nm was detected.