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Synthesis, Properties, and Crystal and Molecular Structure of Chloro[*N*,*N*-bis(2-hydroxyethyl)glycinato]copper(II)

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The crystal and molecular structure of the title copper(II) complex was determined by the X-ray diffraction method. The crystal is orthorhombic with the space group Pbca, $Z=8$, $a=14.18(1)$, $b=15.835(7)$, $c=8.188(3)$ Å. Full matrix least-squares refinements have led to a final R value of 0.047 for 2128 reflections. The copper atom is in a trigonal-bipyramidal geometry, ligated by a nitrogen atom, an oxygen atom of carboxylato group, two hydroxyl oxygen atoms and a chlorine atom. The complex has three five-membered chelate rings which are formed by one copper, one nitrogen, one oxygen, and two carbon atoms. There are two hydrogen bonds formed between the non-coordinated carboxylato oxygen atom and the hydroxyl hydrogen atom. The powder diffuse reflection spectrum of this complex exhibits a band characteristic of trigonal bipyramidal structure at 1000 nm. In the far-infrared absorption spectra of this complex, the bands at 340, 317, and 275 cm^{-1} are assigned to the stretching vibrations of Cu-N, Cu-Cl, and Cu-O (carboxylato), respectively.

Some of the present authors have previously reported on the syntheses and properties of bivalent metal complexes of *N*,*N*-bis(2-hydroxyethyl)glycine (Hbheg).[1] In that work two copper(II) complexes with Hbheg have been prepared; one is $[\mathrm{Cu(bheg)_2}]$ and the other is [CuCl(bheg)].

Anan′eva et al. have determined by an X-ray diffraction study that in the former complex the copper atom occupied the center of inversion and that the coordination number was six in an elongated tetragonal bipyramid formed by two nitrogen atoms and four oxygen atoms from two ligands.[2]

As for the latter complex, it has been presumed that the copper atom is coordinated through an oxygen atom of the carboxylato group, a nitrogen atom and two oxygen atoms of two hydroxyl groups.[1]

However, there are many types of coordination for a hydroxyl group. For example, in the case of bis(triethanolamine)nickel(II) nitrate, the nickel atom is ligated by two oxygen atoms out of the three hydroxyl groups in one triethanolamine molecule, and the other oxygen atom is not associated with the coordination;[3] for bis(triethanolamine)strontium(II) nitrate, three hydroxyl oxygen atoms coordinate the identical strontium atom.[4]

It is therefore difficult to determine from the infrared spectra how these hydroxyl oxygen atoms coordinate the copper atom in [CuCl(bheg)].

In this work, the structure of [CuCl(bheg)] was determined by an X-ray diffraction study; the behavior of the two hydroxyl groups is discussed in detail. In addition, this structure is compared with the structure of copper(II) chloride complex with *N*,*N*-diethylglycine (Hdeg), [CuCl(deg)],[5] previously investigated in our laboratory, and an interpretation of the properties has been carried out based on the proposed structure.

Experimental

Preparation of the Sample. The samples for the X-ray diffraction study were prepared as follows: equimolar amounts of $\mathrm{CuCl_2 \cdot 2H_2O}$ and Hbheg were mixed in aqueous solution. Green crystals were obtained from this solution by keeping it in a desiccator containing ethanol for several days.

X-Ray Measurements and Structure Determination. The crystal data are given in Table 1. The reflection intensities were collected by the ω-2θ scan technique ($2\theta<70°$) on a Rigaku AFC-6A automated four-circle diffractometer, with graphite monochromated Mo$K\alpha$ radiation ($\lambda=0.71073$ Å). The 2128 intensities ($|F_o|>3\sigma(|F_o|)$) were corrected for Lorentz and polarization factors, but not for absorption, because of the low magnitude of $\mu r(<1.0)$.

All calculations were carried out on a Hitachi M-680H computer at the Computer Center of The University of Tokyo, using UNICS III[6] and ORTEP.[7] The scattering factors were taken from tables.[8] The structure was solved by the heavy-atom method. The position of the copper atom was obtained from the three-dimensional Patterson function, while the positions of all other non-hydrogen atoms were successively located by Fourier syntheses and were refined by a block-diagonal least-squares method and only in the last cycle by a full matrix least-squares method. The positions of hydrogen atoms were obtained by difference-Fourier syntheses. In the last cycle of the full matrix least-squares refinement with anisotropic temperature factors for all non-hydrogen atoms, all the parameter shifts were less than one-third of the corresponding standard deviations. The weighting scheme was $W=1/\{a\times(|F_o|)^2+b\times|F_o|+c\}$. These coefficients were automatically computed in the program system. The final R value was 0.047.

Powder Diffuse Reflection and Electronic Spectra. These

Table 1. Crystal Data

$\mathrm{CuCl(C_6H_{12}NO_4)}$	F.W.=261.17
Orthorhombic	Pbca
$a=14.18(1)$ Å	$b=15.835(7)$ Å
$c=8.188(3)$ Å	$U=1838(2)$ Å^3
$Z=8$	
$D_m=1.871(3)$ g cm^{-3}	$D_x=1.887$ g cm^{-3}
$\mu(\mathrm{Mo}K\alpha)=26.6$ cm^{-1}	

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spectra were obtained from 800 to 1500 nm with a JASCO UVIDEC-590 spectrophotometer. The spectra from 400 to 800 nm were obtained with a Hitachi 624 digital spectrophotometer. Both spectrophotometers were equipped with a standard reflection attachment and a magnesium oxide standard for measurements of powder diffuse reflection spectra.

Infrared and Far-Infrared Absorption Spectra. Infrared absorption spectra from 4000 to 400 cm^{-1} were measured using a Hitachi spectrophotometer, type EPI-G$_2$. Far-infrared absorption spectra from 700 to 200 cm^{-1} were measured using a Hitachi spectrophotometer, type EPI-L. Samples were prepared as KBr disks and Nujol mulls. The spectra were calibrated with polystyrene and atmospheric water vapor.

Results and Discussion

Structure of [CuCl(bheg)]. The final atomic parameters are listed in Table 2,[9] the interatomic distances in Table 3,[9] and the bond angles in Table 4.

Table 2. Final Positional Parameters (×10^4) and Equivalent Isotropic Temperature Factors (B_{eq}/Å^2),[a] with the Estimated Standard Deviations in Parentheses[b]

Atom	X	Y	Z	B_{eq}/Å^2
Cu	1237.4(3)	916.0(3)	689.9(4)	2.1
Cl	1066.2(9)	767.5(7)	3349.0(1)	3.4
O(1)	2534(2)	1608(2)	703(4)	2.8
O(2)	213(2)	1844(2)	416(3)	2.1
O(3)	1200(3)	−294(2)	170(3)	3.3
O(4)	1337(2)	−1212(2)	−1831(3)	2.8
N	1384(2)	1065(2)	−1731(3)	1.9
C(1)	2126(3)	1707(3)	−2065(5)	2.8
C(2)	430(3)	1336(3)	−2321(4)	2.3
C(3)	1637(4)	231(2)	−2423(5)	2.6
C(4)	2932(3)	1603(3)	−902(5)	3.1
C(5)	54(4)	2027(3)	−1280(5)	2.7
C(6)	1369(3)	−478(2)	−1288(4)	2.2

a) The equivalent isotropic temperature factors for non-hydrogen atoms were computed using the following expression: $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2)$. B_{ij}'s are in the form: $\exp\{-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2klB_{23}+2hlB_{13}+2hkB_{12})\}$. b) Final atomic parameters of hydrogen atoms are deposited.[9]

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

Cu-Cl	2.203(1)	N-C(1)	1.487(5)
Cu-O(1)	2.140(4)	N-C(2)	1.499(5)
Cu-O(2)	2.078(3)	N-C(3)	1.481(5)
Cu-O(3)	1.963(3)	C(1)-C(4)	1.497(6)
Cu-N	2.007(3)	C(2)-C(5)	1.487(6)
O(1)-C(4)	1.430(5)	C(3)-C(6)	1.505(5)
O(2)-C(5)	1.437(5)	O(1)-H(O1)	0.63(6)
O(3)-C(6)	1.252(4)	O(2)-H(O2)	0.68(4)
O(4)-C(6)	1.246(4)		
O(1)-O(4)$^{\text{I}}$	2.652(4)	O(2)-O(4)$^{\text{II}}$	2.678(4)
O(1)-H(O1)$^{\text{I}}$	2.03(6)	O(2)-H(O2)$^{\text{II}}$	2.00(4)

Key to symmetry operations: I. $0.5-x$, $-y$, $0.5+z$; II. $-x$, $-y$, $-z$. a) Interatomic distances of C-H are deposited.[9]

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

Cl-Cu-O(1)	98.3(1)	Cu-O(3)-C(6)	115.4(2)
Cl-Cu-O(2)	96.03(9)	O(3)-C(6)-O(4)	123.4(3)
Cl-Cu-O(3)	96.15(9)	O(3)-C(6)-C(3)	117.6(3)
Cl-Cu-N	179.29(9)	O(4)-C(6)-C(3)	119.0(3)
O(1)-Cu-O(2)	103.8(1)	Cu-N-C(1)	109.6(2)
O(1)-Cu-O(3)	121.6(2)	Cu-N-C(2)	105.0(2)
O(2)-Cu-O(3)	130.4(1)	Cu-N-C(3)	107.3(2)
O(1)-Cu-N	81.7(1)	C(1)-N-C(2)	112.5(3)
O(2)-Cu-N	83.3(1)	C(1)-N-C(3)	111.6(3)
O(3)-Cu-N	84.4(1)	C(2)-N-C(3)	110.6(3)
Cu-O(1)-C(4)	109.4(3)	O(1)-C(4)-C(1)	106.4(4)
Cu-O(2)-C(5)	110.9(2)	O(2)-C(5)-C(2)	110.5(3)
O(1)-H(O1)··O(4)$^{\text{I}}$	170(7)	O(2)-H(O2)··O(4)$^{\text{II}}$	175(4)

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

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

Plane (1)	[O(1), O(2), O(3)] Cu, 0.2405; Cl, 2.4427; N, −1.7657
Plane (2)	[Cu, O(1), N, C(1), C(4)] Cu, 0.1187; O(1), −0.1683; N, 0.2113; C(1), −0.2771; C(4), 0.2087
Plane (3)	[Cu, O(2), N, C(2), C(5)] Cu, 0.1615; O(2), −0.0106; N, −0.2371; C(2), 0.3006; C(5), −0.1415
Plane (4)	[Cu, O(3), N, C(3), C(6)] Cu, −0.0694; O(3), 0.0492; N, 0.1228; C(3), −0.1291; C(6), 0.0479; O(4), 0.1700
Plane (5)	[O(3), O(4), C(3), C(6)] Cu, 0.0997; O(3), −0.0014; O(4), −0.0014; N, 0.3872; C(3), −0.0011; C(6), 0.0040

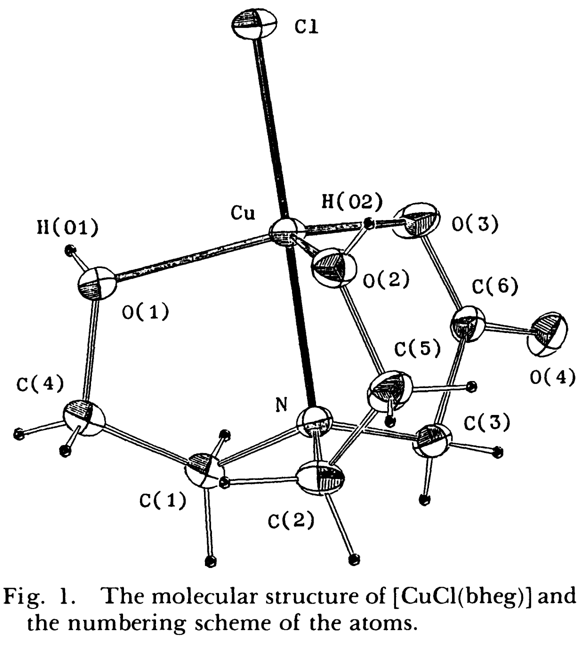

Fig. 1. The molecular structure of [CuCl(bheg)] and the numbering scheme of the atoms.

The deviations of atoms from least-squares planes are shown in Table 5. The molecular structure of the complex and the numbering scheme of the atoms, except alkyl hydrogen atoms, are shown in Fig. 1.

The stucture of the complex is trigonal-bipyramid.

The copper atom is surrounded by five atoms: one carboxylato oxygen atom, two hydroxyl oxygen atoms, one nitrogen atom and one chlorine atom. The nitrogen atom and the chlorine atom are at the apical position. The angle Cl-Cu-N is 179.29(9)° and three coordinated oxygen atoms form a triangle around the copper atom. The copper atom is 0.24 Å above the plane formed by the three ligating oxygen atoms. The bond length of Cu-O (carboxylato) (1.963 Å) is shorter than those of Cu-O (hydroxyl) (2.140 and 2.078 Å).

The complex has three five-membered *N,O*-chelate rings. They are all distorted because of the small N-Cu-O angles. As shown in Table 5, plane (4) shows the least deviation among the chelate rings because it includes one sp^2 carbon atom. All C-C bond lengths are slightly shorter than the usual general C-C bond lengths: this is the same trend as those of the free ligand already reported.[10] The three C-N bonds become shorter than those of the free ligand (1.508, 1.505, and 1.504 Å) because the nitrogen atom of the free ligand is protonated. The distances between carboxylato carbon atom and carboxylato oxygen atom: C(6)-O(3) (coordinated); 1.252(4) Å and C(6)-O(4) (non-coordinated), 1.246(4) Å, are not so different, since O(4) forms two hydrogen bonds with the neighboring unit. The bond lengths of the O-H are shorter than the usual general O-H bond lengths. The free ligand also has the same trend.[10]

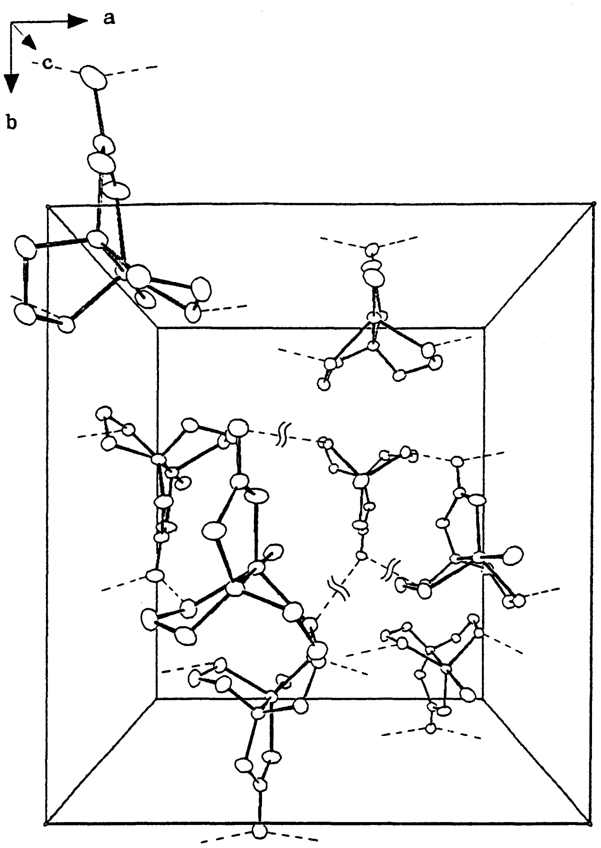

Fig. 2. The crystal structure of [CuCl(bheg)]. (----: Hydrogen bonding).

Let us now compare the structure of this complex with that of [CuCl(deg)]. The coordination number of [CuCl(deg)] is five,[5] like that of [CuCl(bheg)]. In [CuCl(deg)], the copper atom is surrounded by three carboxylato oxygen atoms, one nitrogen atom, and one chlorine atom, and the structure consists of a one-dimensional polymer chain bridged by only one carboxylato group of *N*,*N*-diethylglycine. This [CuCl(bheg)] has no bridging carboxylato groups and so is a monomer with the coordination of hydroxyl groups.

The molecular packing of the complex is shown in Fig. 2. There are no intermolecular interactions except at the two hydrogen bonds, which are formed between the non-coordinated carboxylato oxygen atom and the hydroxyl hydrogen atom. They are parallel to the ac plane. No intermolecular interactions parallel to b axis are found. This agrees with the easy cleavage of this crystal along this axis.

Powder Diffuse Reflection and Electronic Spectra. The reflection spectrum shows a broad band at about 1000 nm. This wavelength is different from those of copper(II) chloride complexes with *N*-substituted amino acids previously investigated in our laboratory, as shown in Table 6, but it is near to the value of the reflection band (900 nm) for 1-(2-ammonioethyl)piperazinediium pentachlorocuprate-(II) dihydrate, which has a typical trigonal bipyramidal structure.[14] The electronic spectrum in aqueous solution shows a band at 760 nm. As this spectrum is similar to that of octahedral configurations, the structure of this complex seems to change in aqueous solution.

Infrared Absorption Spectra. There is a strong broad band at 3025 cm^{-1} for [CuCl(bheg)]. It is assigned to the OH stretching vibration, because of its disappearance on deuteration and the absence of bands in this region for [CuCl(deg)]. As this band is observed at a lower frequency region than for the free ligand (3186 and 3089 cm^{-1}), the strengths of the O-H bonds seem to become weaker on coordination.

For the free ligand, the COO^- antisymmetric and symmetric stretching vibrations appear at 1639 and 1401 cm^{-1}, respectively. In [CuCl(bheg)] the former

Table 6. Powder Diffuse Reflection Spectra of Copper(II) Chloride Complexes with *N*-Substituted Amino Acids

Complex	λ/nm	Coordination number[a]	Reference
CuCl(pro)·MeOH	754	5+1	11
CuCl(hpro)·H_2O	755	5+1	12
CuCl(pro)·H_2O	730	5	13
CuCl(deg)	626	4+1	5
CuCl(bheg)	1000	5	This work

Hpro=L-proline, Hhpro=4-hydroxy-L-proline. a) Coordination Number: For example "5+1" stands for that the complex has 5 usual coordination bonds and 1 weak bond.

shifts to a somewhat lower frequency region (1578 cm^{-1}) and the latter shifts to a higher one (1406 cm^{-1}). The frequency separation between these two frequencies for [CuCl(bheg)] (172 cm^{-1}) is smaller than that of the free ligand. It has been reported that the frequency separation betweeen the two COO$^-$ stretching vibrations in an unidentate complex is generally larger than that of a free ligand.[15] Though [CuCl(bheg)] shows an opposite tendency, this vibrational spectrum pattern is consistent with the result of X-ray analyses that the bond lengths of the C-O (coordinated) and the C-O (non-coordinated) are almost the same.

Far-Infrared Absorption Spectra. Two new bands (340 and 275 cm^{-1}) which were not observed in the ligand appear in [CuCl(bheg)]. They are assigned to Cu-N and Cu-O (carboxylato) stretching vibrations, by comparing this spectrum with those of [Cu(bheg)$_2$] and metal complexes with other amino acids.[16-18] From the molecular structure determined by X-ray analysis, it is clear that this molecule has a Cs symmetry. Therefore in view of the five atoms which form a trigonal-bipyramid around the copper atom, there are twelve normal vibrations. They are divided into two symmetries (8A′+4A″) which are all infrared active. Since the bond lengths of the Cu-OH are longer than that of Cu-O (carboxylato), two Cu-OH stretching vibrations appear at a lower frequency region than where Cu-O (carboxylato) stretching vibration is observed. Therefore, it is reasonable to assign the band at 275 cm^{-1} to the Cu-O (carboxylato) stretching vibration.

The band at 317 cm^{-1} is assigned as a terminal Cu-Cl stretching vibration, by comparison with the spectra of [Cu(bheg)$_2$], [CuCl(deg)][5] (344 cm^{-1}) and other copper(II) complexes containing chlorine atoms.[19,20]

Such behavior in infrared and far-infrared spectra is in good agreement with the results of X-ray diffraction study of [CuCl(bheg)].

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