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Synthesis, Properties, and Crystal and Molecular Structure of *N,N*-Bis(2-hydroxyethyl)glycinato Copper(II) Perchlorate Monohydrate

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Abstract

The synthesis and X-ray diffraction study of the title copper(II) complex have been carried out. The crystal is monoclinic with the space group $P2_1/n$, $Z = 4$, $a = 12.646(2)$, $b = 9.369(1)$, $c = 10.619(2)$ Å, $\beta = 108.69(1)°$. Full matrix least-squares refinements have led to a final R value of 0.052 for 2996 reflections. The ligand coordinates to the copper atom so as to form three five-membered chelate rings. The copper atom is in a trigonal-bipyramidal geometry, ligated by a nitrogen atom, a carboxylato oxygen atom, two hydroxyl oxygen atoms and a carboxylato oxygen atom of the neighboring unit. The complex forms a one-dimensional polymer chain through the carboxylato group and is charged positively. The perchlorate ion does not coordinate to the copper atom and is located within a bundle of the polymer chains of the complex. Some properties of the complex are discussed.

Introduction

Among the studies of the copper(II) complexes with amino acids and *N*-substituted amino acids are included some syntheses and structure determinations which have been carried out by the present authors [1–3]. This investigation is part of that program. In *N,N*-bis(2-hydroxyethyl)glycine (Hbheg), two hydroxyl oxygen atoms coordinate to the copper atom, in addition to a nitrogen atom and carboxylato oxygen atoms. In fact, it has been reported that in its halogeno complexes [CuCl(bheg)] and [CuBr(bheg)] the copper atom is surrounded by five ligating atoms so as to form a trigonal-bipyramid [4, 5]. A carboxylato oxygen atom and two hydroxyl oxygen atoms form a triangle around the copper atom, and a halogen atom and a nitrogen atom are at the apical positions.

In that case, the halide ion is coordinated to the copper atom, in addition to its original purpose of neutralizing the charge of the complex. So we were motivated to investigate the effects on coordination to the copper atom due only to the *N,N*-bis(2-hydroxyethyl)glycinate anion ($bheg^-$).

There are at least two ways to achieve this. One is the synthesis and the investigation of $[Cu(bheg)_2]$. It has already been reported that $[Cu(bheg)_2]$ is a normal hexa-coordinate complex ligated by two nitrogen atoms and four oxygen atoms [6]. The other way is the synthesis of [Cu(bheg)]X (X: any counter ion). In this case, we used a perchlorate ion as the negatively charged counter ion, because it usually does not coordinate to a metal ion in aqueous solution [7].

In this work, the structure of $[Cu(bheg)]ClO_4 \cdot H_2O$ was determined by X-ray diffraction. The behavior of the ligand is discussed in detail. In addition, this structure and other physical properties are compared with those of [CuCl(bheg)] samples previously studied in our laboratory.

Experimental

Preparation of the Sample

The samples for the X-ray diffraction study were prepared as follows. Equimolar amounts of $Cu(ClO_4)_2 \cdot 6H_2O$ and Hbheg were mixed in aqueous solution, then each sample was condensed at 60–70 °C for several hours until it became syrupy. Pale blue crystals were obtained from this solution by keeping it for several days. *Anal.* Found: C, 21.05; H, 3.95; N, 4.13; Cl, 10.34. Calc. for $Cu(C_6H_{12}NO_4)ClO_4 \cdot H_2O$: C, 21.00; H, 4.11; N, 4.08; Cl, 10.33%. The results of the elemental analyses alone, however, give no evidence whether a perchlorate ion and a water molecule coordinate to the copper atom or not.

X-ray Measurements and Structure Determination

The crystal data are given in Table 1. The reflections were collected by the ω–2θ scan technique ($2\theta < 70°$) on a Rigaku AFC-5 automated four-circle diffractometer, with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The 2996 intensities

0020-1693/89/$3.50

TABLE 1. Crystal data

$Cu(bheg)ClO_4 \cdot H_2O$
Formula weight = 343.18
Monoclinic
$P2_1/n$
$a = 12.646(2)$ Å
$b = 9.369(1)$ Å
$c = 10.619(2)$ Å
$\beta = 108.69(1)^\circ$
$Z = 4$
$V = 1191.7(3)$ Å^3
$D_m = 1.901(1)$ g cm^{-3}
$D_x = 1.912$ g cm^{-3}
μ(Mo Kα) = 21.0 cm^{-1}

($|F_o| > 3\sigma(|F_o|)$) were corrected for Lorentz and polarization factors, but not for absorption, because of the low magnitude of $\mu r (< 1.0)$.

The structure was solved by the direct method and refined by a block diagonal least-squares method, except for the last 5 cycles. For these last 5 cycles, it was refined by the full matrix least-squares method. The positions of the water molecule and hydrogen atoms were obtained by difference-Fourier syntheses. In the anisotropic temperature factors for all non-hydrogen atoms, all the parameter shifts were less than one-third of the corresponding standard deviations. The final $R = [(\Sigma||F_o| - |F_c||)/\Sigma|F_o|]$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ values were 0.052 and 0.072 respectively.

All calculations were carried out on a Hitachi M-682H computer at the Computer Center of the University of Tokyo, using UNICS III [8], MULTAN [9] and ORTEP [10]. The scattering factors were taken from ref. 11.

Powder Diffuse Reflection and Electronic Spectra

These spectra were obtained from 800 to 1400 nm with a Jasco UVIDEC-590 spectrophotometer. The spectra from 370 to 800 nm were obtained with a Hitachi 624 digital spectrophotometer. Both spectrophotometers were equipped with a standard reflection attachment for powder diffuse reflection spectra. The electronic spectra of the aqueous solution were also measured.

Infrared Absorption Spectra

Infrared absorption spectra from 4000 to 400 cm^{-1} were measured using a Jasco IR-810 spectrophotometer. Samples were prepared as KBr disks.

Magnetic Study

The magnetic moment of this complex was obtained for the solid samples by the Gouy method, using $Hg[Co(SCN)_4]$ as the calibration standard at 22.9 °C.

Results and Discussion

Structure of [Cu(bheg)]ClO$_4$·H$_2$O

The final atomic parameters are listed in Table 2, the interatomic distances in Table 3, and the bond angles in Table 4. The crystal structure of the complex is shown in Fig. 1.

As shown in Fig. 1, neither the perchlorate ion nor the water molecule coordinate to the copper atom. So the perchlorate ion is a counter ion and the water is water of crystallization. As a result of the X-ray diffraction study, the exact molecular formula of the complex was determined to be $[Cu(bheg)]ClO_4 \cdot H_2O$; thus the complex charges positively.

TABLE 2. Final positional parameters (×10^4) and equivalent isotropic temperature factors, B_{eq} (Å^2), with estimated standard deviations in parentheses

Atom	x	y	z	B_{eq} (Å^2)
Cu	1773.7(3)	2462.8(4)	2501.9(5)	2.5
O(1)	1986(3)	1459(4)	4421(3)	3.9
O(2)	605(2)	1295(3)	1158(3)	3.2
O(3)	2420(2)	4424(2)	2803(3)	2.9
O(4)	1851(2)	6693(2)	2597(3)	3.1
N	474(2)	3395(3)	2866(3)	2.5
C(1)	679(4)	3272(4)	4325(5)	3.6
C(2)	1032(5)	1794(5)	4819(5)	4.0
C(3)	−578(3)	2668(4)	2071(4)	3.1
C(4)	−430(3)	2062(5)	832(5)	3.6
C(5)	508(3)	4907(3)	2488(5)	3.2
C(6)	1691(3)	5365(3)	2667(4)	2.5
Cl	2350(1)	3041(1)	−910(1)	3.6
O(Cl1)	2289(6)	1556(5)	−944(1)	10.5
O(Cl2)	1676(4)	3620(5)	−166(5)	6.5
O(Cl3)	3441(4)	3463(6)	−245(6)	8.0
O(Cl4)	1991(6)	3597(9)	−2208(5)	10.1
O(W)	193(4)	9003(4)	2313(4)	4.6

TABLE 3. Selected bond lengths, l (Å) with estimated standard deviations in parentheses

Cu–O(1)	2.181(4)	C(1)–C(2)	1.494(7)
Cu–O(2)	2.016(3)	C(3)–C(4)	1.497(7)
Cu–O(3)	1.995(3)	C(5)–C(6)	1.508(5)
Cu–O(4)^{I}	1.916(3)	O(1)–H(O1)	0.80(7)
Cu–N	2.003(3)	O(2)–H(O2)	0.70(6)
O(1)–C(2)	1.434(8)	Cl–O(Cl1)	1.399(5)
O(2)–C(4)	1.434(5)	Cl–O(Cl2)	1.439(6)
O(3)–C(6)	1.251(4)	Cl–O(Cl3)	1.388(4)
O(4)–C(6)	1.265(4)	Cl–O(Cl4)	1.403(6)
N–C(1)	1.491(6)	O(W)^{II}---H(O2)	1.92(6)
N–C(3)	1.493(4)	O(W)^{II}---O(2)	2.603(5)
N–C(5)	1.478(4)		

Key to symmetry operations: I, $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; II, $x, -1 + y, z$.

TABLE 4. Selected bond angles, ϕ (°) with estimated standard deviations in parentheses

$O(4)^I$–Cu–N	171.4(1)	O(1)–C(2)–C(1)	106.6(5)
O(1)–Cu–O(2)	105.6(1)	O(2)–C(4)–C(3)	109.8(3)
O(1)–Cu–O(3)	109.0(1)	O(3)–C(6)–C(5)	118.5(3)
O(2)–Cu–O(3)	141.5(1)	O(3)–C(6)–O(4)	125.0(3)
O(1)–Cu–N	82.5(1)	O(4)–C(6)–C(5)	116.4(3)
O(2)–Cu–N	85.0(1)	N–C(1)–C(2)	111.6(4)
O(3)–Cu–N	83.5(1)	N–C(3)–C(4)	109.3(4)
Cu–O(1)–C(2)	108.5(3)	N–C(5)–C(6)	110.6(3)
Cu–O(2)–C(4)	107.7(3)	O(2)–H(O2)---O(W)	170(6)
Cu–O(3)–C(6)	112.5(2)		
Cu–$O(4)^I$–$C(6)^I$	125.0(3)		
Cu–N–C(1)	106.8(2)		
Cu–N–C(3)	109.3(2)		
Cu–N–C(5)	105.6(3)		

Key to symmetry operation: I, $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$.

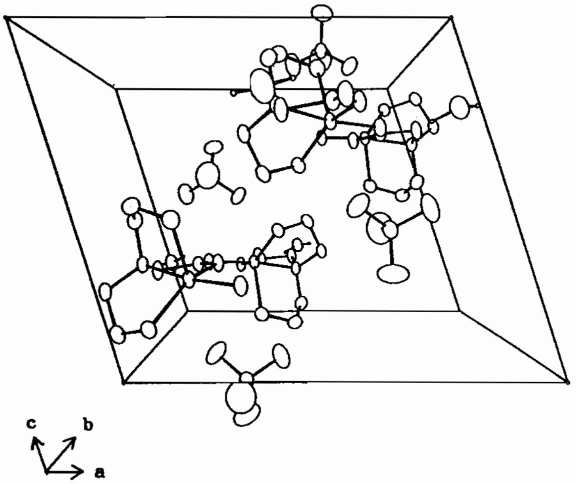

Fig. 1. The crystal structure of [Cu(bheg)]ClO$_4$·H$_2$O.

The structure of the complex ion [Cu(bheg)]$^+$ and the numbering scheme of the atoms, except for the hydrogen atoms bonding to the carbon atom, are shown in Fig. 2. The form shown in Fig. 2, without $O(4)^I$, is considered as one unit of the complex in this discussion. As shown in Fig. 2, the copper atom is surrounded by five atoms: one carboxylato oxygen atom, two hydroxyl oxygen atoms, one nitrogen atom and one carboxylato oxygen atom of the neighboring unit. O(1), O(2), O(3) and N are ligating to the same copper atom so as to form three five-membered chelate rings. Each ring consists of one copper atom, one carboxylato or hydroxyl oxygen atom, one nitrogen atom and two carbon atoms. In addition, since $O(4)^I$ is coordinating to the copper, the complex forms a trigonal-bipyramid. In other words, the ligand is coordinating to two copper atoms as a pentadentate ligand.

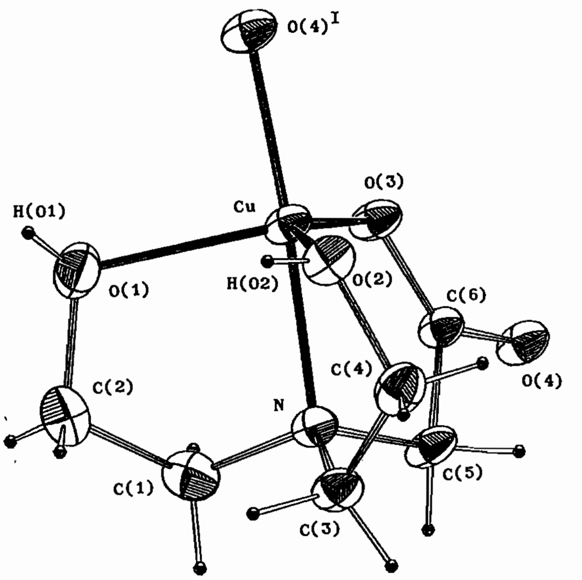

Fig. 2. The molecular structure of [Cu(bheg)]$^+$ and the numbering scheme of the atoms. Key to symmetry operation: I, $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$.

O(1), O(2) and O(3) form a triangle around the copper atom. The copper atom is 0.22 Å above the plane(1) formed by those three oxygen atoms. N and $O(4)^I$ are at the apical positions. The angle $O(4)^I$–Cu–N is 171.4(1)°. The angle between the vector from $O(4)^I$ to N and plane(1) is 82.94°. And the vector from N to Cu is almost vertical (88.17°). So the trigonal-bipyramidal geometry is slightly distorted. The bond lengths of all C–C bonds and of the two O(hydroxyl)–H bonds are slightly shorter than the usual values. These are the same trends as those found for [CuCl(bheg)] and for the free ligand [12].

The Cu–O and Cu–N distances of [Cu(bheg)]$^+$ and [CuCl(bheg)] are listed in Table 5. The Cu–O(carboxylato) distances (1.995 and 1.916 Å) are shorter than those of Cu–O(hydroxyl) (2.181 and 2.016 Å). But the differences between Cu–O(2) (2.016 Å) and Cu–O(3) (1.995 Å) are quite small.

In general, Cu–O(carboxylato) distances are significantly shorter than Cu–O(hydroxyl) distances because of the difference between the electron density of hydroxyl oxygen (neutral) and that of carboxylato oxygen (rather ionic).

Therefore the strength of the bond Cu–O(3) is weaker than that of the usual one. This fact is due to the presence of the bond between Cu(neighboring unit) and O(4). In [CuCl(bheg)], the coordination of the O(4) is impossible, because the presence of the chlorine atom prevents O(4) from coordinating to the copper atom. In this complex, the Cu–O(4) distance is shorter than the Cu–O(3) distances. The interesting thing is that the bond bridging to the

TABLE 5. Cu–O bond distances, *l* (Å) of [Cu(bheg)]$^+$ and [CuCl(bheg)]

Complex	Cu–O(1)	Cu–O(2)	Cu–O(3)	Cu–O(4)^{I}	Cu–N
[Cu(bheg)]$^+$	2.181	2.016	1.995	1.916	2.003
[CuCl(bheg)]	2.140	2.078	1.963		2.007

Key to symmetry operation: I, $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$.

neighboring copper atom (Cu–O(4)) is stronger than the chelating bond (Cu–O(3)). There is a similar example in the copper(II) complex of nitrilotriacetic acid [13]. In that complex, the Cu–O distances bonding to the neighboring copper are 1.958 and 1.989 Å, and those in the chelate rings are 2.351 and 2.297 Å, respectively. The strength of the bond Cu–O(4) may correspond to that of the bond Cu–O(3) of [CuCl(bheg)]; the former bond is also shorter. This trend is responsible for the lower repulsion at the apical site above the copper atom. Because the copper atom is slightly above the triangle plane(1) formed by three oxygen atoms, the repulsions from these oxygen atoms are weaker. Thus the site occupied by O(4) is more stable for coordination than the site of O(3). But the bond length of O(4)–C(6) (1.265 Å) is longer than that of O(3)–C(6) (1.251 Å). The structure of the complex cation consists of a one-dimensional polymer chain bridged by the carboxylato group with *syn-* and *anti-* geometry. This polymer chain is parallel to the *b* axis, as shown in Fig. 3. There are two polymer chains through a unit cell. One direction bonding to the neighboring unit is the reverse of the other.

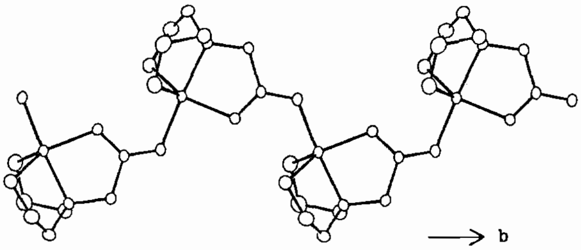

Fig. 3. The polymer chain of [Cu(bheg)]$^+$.

The perchlorate ion and water molecule are located within the bundle of polymer chains. As there are no definite bonds between the perchlorate oxygen atoms and any specific atoms of the polymer chain, the bond between the chain and the perchlorate ion is ionic. In addition to this fact, there is no attraction similar to hydrogen bonding between these chains. In other words, the polymer chains are bundled together due only to the ionic bonds between the positive charges of the chains of the complex and the negative charges of the perchlorate ions.

The perchlorate oxygen atoms are disordered and have high temperature factors. There is only one hydrogen bond between the water molecule and H(O2).

Powder Diffuse Reflection and Electronic Spectra

The reflection spectrum shows a broad band at about 900 nm. This wavelength differs slightly from that of [CuCl(bheg)] (1000 nm). The difference between [Cu(bheg)]$^+$ and [CuCl(bheg)] may be due to the difference of the kind of ligating atoms. The ligating atoms of this complex are four oxygen atoms and one nitrogen atom, and those of [CuCl(bheg)] are one chlorine atom, three oxygen atoms and one nitrogen atom.

The electronic spectrum of aqueous solution shows a band at 760 nm. This is the same as that of [CuCl(bheg)] and is similar to that found for octahedral configurations. Therefore these complexes seem to have similar structures or the same structure in aqueous solution, where the water molecule as well as the ligating atoms of Hbheg coordinate to the copper atom.

Infrared Absorption Spectra

A strong broad band is found at 3021 cm^{-1}: this is assigned to the OH stretching vibration, because [CuCl(bheg)] has a band at the same region (3025 cm^{-1}) which disappears on deuteration. This band is observed at a lower frequency region than that of the free ligand.

In this complex, the bands at 1576 and 1400 cm^{-1} are assigned to the COO$^-$ antisymmetric and symmetric stretching vibrations, respectively. Both bands shift to a lower frequency region than those of free ligand (1639 and 1401 cm^{-1}). The frequency separation of these two bands is 176 cm^{-1}, which is smaller than that of the free ligand. This value is almost the same as that of [CuCl(bheg)] (172 cm^{-1}) and is in good agreement with those of bridging complexes with acetic acid [14]. As for [Cu(bheg)]$^+$ the two C–O bond lengths of the carboxylato group, which behaves as a bidentate group, are the same as those of [CuCl(bheg)]. In [CuCl(bheg)], the bond lengths of C–O(coordinated and non-coordinated) in the carboxylato group are almost the same, though this group works as a unidentate one. This result for the carboxylato group in [CuCl(bheg)] is due to the two hydrogen bonds with the non-coordinated carboxylato oxygen atom in a neighboring molecule.

The four strong bands (1144, 1113, 1089 and 1052 cm^{-1}) are assigned to Cl–O stretching vibrations of the perchlorate ion by comparing with the spectra of $Cu(ClO_4)_2 \cdot 6H_2O$ and other references [15], as their intensities are strong and similar to each other. Few such splits have been observed, because the perchlorate ion is out of coordination and generally has *Td* symmetry [15]. In this case the four Cl–O distances (1.399, 1.440, 1.388 and 1.403 Å) are considerably different from each other because of the effect of the crystalline state and the disorder in the oxygen atoms of the perchlorate ion. These facts are enough to lower the *Td* symmetry [16]. No hydrogen bond whose distance is shorter than 2.2 Å can be found around the perchlorate ion.

Magnetic Moment

The magnetic moment of this complex is 1.84 BM. This value corresponds to that of a normal bivalent copper complex, and is close to that of [CuCl(bheg)] (1.91 BM) and [CuBr(bheg)] (1.88 BM). So there seems to be no magnetic interaction between copper atoms.

Supplementary Material

Observed and calculated structure factors, anisotropic thermal parameters, hydrogen-atom coordinate and the deviation of atoms from least-squares planes are available from the authors on request.

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