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

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Abstract

The crystal and molecular structure of the title copper(II) complex was determined by the X-ray diffraction method. The crystal is monoclinic with the space group *Cc*, $Z = 4$, $a = 14.567(2)$, $b = 6.970(1)$, $c = 11.051(2)$ Å, $\beta = 93.67(1)°$. Full matrix least-squares refinements have led to a final *R* value of 0.057 for 1080 reflections. The copper atom is ligated by one carboxylato oxygen atom, two hydroxyl oxygen atoms and one nitrogen atom of the ligand, and one nitrogen atom and one sulfur atom of the isothiocyanate ion. The copper atom is at the center of the typical tetragonal-bipyramidal geometry. One hydroxyl oxygen atom and sulfur atom are at the apical positions and their bond lengths to the copper atom are longer than usual. The other four atoms form a square around the copper atom. The complex forms a one-dimensional polymer chain through the isothiocyanate ion.

Introduction

As *N*,*N*-bis(2-hydroxyethyl)glycine (Hbheg) has two hydroxyl oxygen atoms and one carboxyl oxygen atom and one nitrogen atom, it can coordinate to a metal ion as a tetradentate ligand. We previously reported the structures of [CuCl(bheg)] [1] and [Cu(bheg)]ClO_4 [2].

In [CuCl(bheg)] a carboxylato oxygen atom and two hydroxyl oxygen atoms form a triangle around the copper atom, and a chlorine atom and a nitrogen atom are at the apical positions, while in [Cu(bheg)]ClO_4 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 neighbouring unit. The complex forms a one-dimensional polymer chain through the carboxylato group and is charged positively.

In this work, the structure of [Cu(bheg)NCS]·H_2O was determined by X-ray diffraction in order to discuss how the isothiocyanate anion acts as a substitute for the chloride ion.

Experimental

Preparation of the Sample

Equimolar amounts of [CuCl(bheg)] and KSCN were dissolved in a H_2O/EtOH (1/1) mixture. A gray precipitate was obtained immediately. This precipitate was washed by the same mixed solvent several times and then washed by ethanol. The precipitate was recrystallized in ethanol solution. Blue crystals were obtained from this solution. *Anal.* Found: C, 27.56; H, 4.65; N, 9.15. Calc. for $Cu(C_6H_{12}NO_4)$-$NCS(H_2O)$: C, 27.85; H, 4.68; N, 9.28%.

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). Out of 3339 independent reflections the 1080 intensities ($|F_o|) > 3\sigma(|F_o|$) with $|F_o| > 10$ were corrected for Lorentz and

TABLE 1. Crystal data of [Cu(bheg)NCS]·H_2O

Formula	$CuC_7H_{14}N_2O_5S$
Formula weight	301.81
Crystal form	monoclinic
Space group	C_c
a (Å)	14.567(2)
b (Å)	6.970(1)
c (Å)	11.051(2)
β (°)	93.67(1)
U (Å^3)	1119.7(3)
Z	4
D_m (g cm^{-3})	1.786(2)
D_x (g cm^{-3})	1.790
μ(Mo Kα) (cm^{-1})	21.4

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polarization factors, but not for absorption, because of the low magnitude of $\mu r(1.0)$.

The structure was solved by the heavy-atom method. The position of the copper atom was obtained from the three-dimensional Patterson function. After then the positions of all other non-hydrogen atoms were successively located by Fourier syntheses and were refined by a full matrix least-squares method. The positions of the water molecule and hydrogen atoms were obtained by difference-Fourier syntheses. The isotropic temperature factors of the hydrogen atoms were assumed to be 4.0 Å^2. In the anisotropic temperature factors for all the non-hydrogen atoms, all the parameter shifts were less than one-third of the corresponding standard deviations. The final R and R_w values were 0.057 and 0.062, respectively; $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

All calculations were carried out on a Hitachi M-682H computer at the Computer Center of the University of Tokyo, using UNICS III [3] and ORTEP [4]. The scattering factors were taken from ref. 5.

Physical Measurements

Infrared absorption spectra, powder diffuse reflection spectra and magnetic moments were obtained by the same methods used for [CuCl(bheg)] [1] and [Cu(bheg)]ClO_4 [2].

Results and Discussion

Structure of [Cu(bheg)NCS]·H_2O

The final atomic parameters are listed in Table 2, the interatomic distances in Table 3 and the bond angles in Table 4. The molecular structure of the complex and the numbering scheme of the atoms, except the alkyl hydrogen atoms, are shown in Fig. 1.

As shown in Fig. 1, the copper atom is surrounded by six atoms; one carboxylato oxygen atom, two hydroxyl oxygen atoms, one nitrogen atom of bheg, one isothiocyanato nitrogen atom and the isothiocyanato sulfur atom of the neighboring unit.

The bond lengths of Cu–O(1) (hydroxyl, 2.37(1) Å) and Cu–S (3.11(1) Å) are longer than those of Cu–O(2) (hydroxyl, 1.98(1) Å), Cu–O(3) (1.98(1) Å), Cu–N(1) (2.01(1) Å) and Cu–N(2) (1.93(1) Å). In $Cu(en)_2(SCN)_2$ the bond Cu–S is extremely weak (3.27 Å) completing a (4 + 2)-coordination group [6]. So this complex has a tetragonal-bipyramidal geometry. The copper atom is 0.05 Å out of the plane which is formed by O(2), O(3), N(1) and N(2).

The three five-membered N,O-chelate rings are formed as in other complexes [1, 2]. In this complex the bond length of Cu–O(2) is the same as that of Cu–O(3) (1.98(1) Å), although the bond length of Cu–O(hydroxyl) is usually longer than that of Cu–O(carboxylato) in [CuCl(bheg)] and [Cu(bheg)]ClO_4.

TABLE 2. Final positional parameters with e.s.d.s in parentheses and equivalent isotropic temperature factors (B_{eq} (Å^2)) of [Cu(bheg)NCS]·H_2O

Atom	x	y	z	B_{eq} (Å^2)
Cu	0.2500	0.2162(2)	0.2500	2.1
O(1)	0.3773(7)	0.3260(12)	0.3753(8)	3.1
O(2)	0.1645(7)	0.4321(14)	0.2702(9)	3.0
O(3)	0.3335(6)	0.0248(13)	0.1823(8)	2.7
O(4)	0.4268(6)	−0.0169(14)	0.0347(9)	3.7
N(1)	0.3036(6)	0.4003(14)	0.1340(9)	2.1
C(1)	0.3751(8)	0.5190(18)	0.1999(11)	2.1
C(2)	0.4366(8)	0.4033(20)	0.2897(13)	2.9
C(3)	0.2285(11)	0.5185(21)	0.0842(13)	3.2
C(4)	0.1711(10)	0.5885(20)	0.1832(15)	3.3
C(5)	0.3476(8)	0.2817(22)	0.0385(11)	3.0
C(6)	0.3717(7)	0.0806(17)	0.0878(10)	2.1
S	0.0997(2)	−0.0745(6)	0.5593(3)	4.0
N(2)	0.1977(9)	0.0563(17)	0.3709(11)	3.1
C(7)	0.1569(8)	0.0059(17)	0.4471(10)	2.1
O(W)	0.4951(7)	−0.1149(17)	0.3249(10)	4.0

TABLE 3. Selected interatomic distances (Å) with e.s.d.s in parentheses of [Cu(bheg)NCS]·H_2O

Cu–S^I	3.11(1)	N(1)–C(1)	1.48(2)
Cu–O(1)	2.37(1)	N(1)–C(3)	1.45(2)
Cu–O(2)	1.98(1)	N(1)–C(5)	1.52(2)
Cu–O(3)	1.98(1)	C(1)–C(2)	1.53(2)
Cu–N(1)	2.01(1)	C(3)–C(4)	1.50(2)
Cu–N(2)	1.93(1)	C(5)–C(6)	1.54(2)
O(1)–C(2)	1.43(2)	O(1)–H(O1)	0.95(16)
O(2)–C(4)	1.46(2)	O(2)–H(O2)	0.75(17)
O(3)–C(6)	1.28(2)	S–C(7)	1.64(1)
O(4)–C(6)	1.23(2)	N(2)–C(7)	1.12(2)
O(2)···O(W)^{II}	2.60(2)	O(2)···H(W1)^{II}	2.06(18)
O(W)^{II}···H(O2)	1.86(17)		

Asymmetric unit: ^{I} $x, -y, -0.5 + z$; ^{II} $-0.5 + x, 0.5 + y, z$.

In the carboxylato functional group, the two C–O bonds (coordinated and non-coordinated) are remarkably different, the C(6)–O(3) being longer than C(6)–O(4). This is a different trend from [CuCl(bheg)].

For isothiocyanato, the nitrogen atom is coordinating to one copper atom and the sulfur atom is coordinating to another copper atom. So the copper atoms are connected by a bridge of isothiocyanato. The bond angle of C(7)–S–Cu(neighboring unit) is 104.7(4)°. The isothiocyanate ion is almost a linear molecule because the bond angle of N(2)–C(7)–S is 178(1)°.

The crystal structure of [Cu(bheg)NCS]·H_2O is shown in Fig. 2 and the polymer chain of complexes

TABLE 4. Selected bond angles (°) with e.s.d.s in parentheses of [Cu(bheg)NCS]·H_2O

S^{I}–Cu–O(1)	172.4(4)	O(3)–C(6)–O(4)	124(1)
S^{I}–Cu–O(2)	84.1(3)	O(3)–C(6)–C(5)	118(1)
S^{I}–Cu–O(3)	87.2(3)	O(4)–C(6)–C(5)	119(1)
S^{I}–Cu–N(1)	93.1(3)	Cu–N(1)–C(1)	109.4(7)
S^{I}–Cu–N(2)	89.8(4)	Cu–N(1)–C(3)	106.9(8)
O(1)–Cu–O(2)	99.4(4)	Cu–N(1)–C(5)	107.2(8)
O(1)–Cu–O(3)	87.8(3)	C(1)–N(1)–C(3)	111(1)
O(2)–Cu–O(3)	164.0(4)	C(1)–N(1)–C(5)	109.3(9)
O(1)–Cu–N(1)	81.1(3)	C(3)–N(1)–C(5)	113(1)
O(1)–Cu–N(2)	96.4(4)	O(1)–C(2)–C(1)	106(1)
O(2)–Cu–N(1)	81.9(4)	O(2)–C(4)–C(3)	108(1)
O(2)–Cu–N(2)	94.7(5)	N(1)–C(1)–C(2)	113(1)
O(3)–Cu–N(1)	85.2(4)	N(1)–C(3)–C(4)	111(1)
O(3)–Cu–N(2)	98.7(5)	N(1)–C(5)–C(6)	110(1)
N(1)–Cu–N(2)	175.3(5)		
Cu–O(1)–C(2)	102.7(7)	S–C(7)–N(2)	178(1)
Cu–O(2)–C(4)	115.2(8)	C(7)–S–Cu^{II}	104.7(4)
Cu–O(3)–C(6)	114.5(8)	Cu–N(2)–C(7)	163(1)
O(2)···H(W1)^{III}–O(W)^{III}		136(18)	
O(2)–H(O2)···O(W)^{III}		169(18)	

Asymmetric unit: ^{I} x, $-y$, $-0.5+z$; ^{II} x, $-y$, $0.5+z$; ^{III} $-0.5+x, 0.5+y, z$.

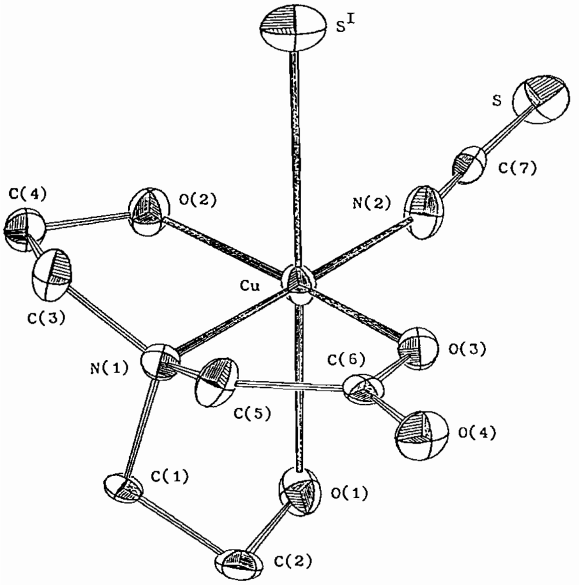

Fig. 1. Molecular structure of [Cu(bheg)NCS]. Asymmetric unit: ^{I} $x, -y, -0.5+z$.

is shown in Fig. 3. The water molecule is in a unit cell as a lattice water. No intermolecular interaction, except hydrogen bonding, is found between the complex and the water molecule.

The complexes form a one-dimensional polymer chain bridged by the isothiocyanato. The polymer chains are parallel to the c axis.

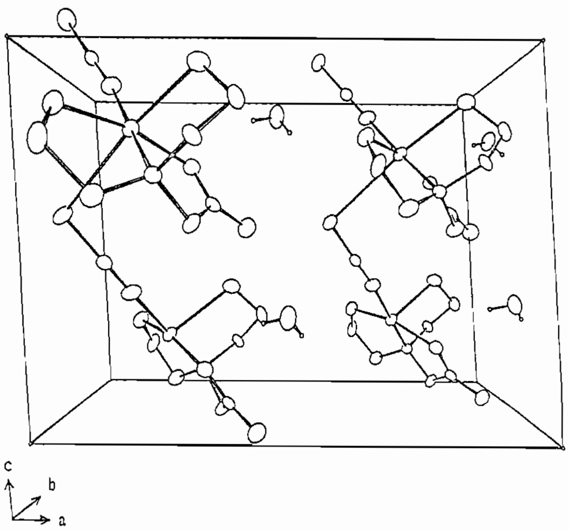

Fig. 2. Crystal structure of [Cu(bheg)NCS]·H_2O.

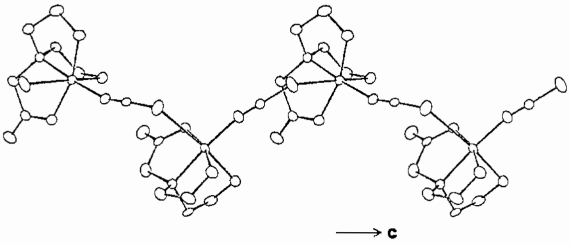

Fig. 3. Polymer chain of [Cu(bheg)NCS].

Infrared Absorption Spectra

The band at 3226 cm^{-1} and the broad band near 3000 cm^{-1} are assigned to OH stretching vibrations. The former band is observed at the higher frequency region as compared with those of [CuCl(bheg)] (3025 cm^{-1}) and [Cu(bheg)]ClO_4 (3021 cm^{-1}). But this assignment is reasonable, because Cu–O(1) (2.37 Å) is the longest of all the other Cu–O (hydroxyl group) bond lengths: 1.98 Å for this complex, 2.140 and 2.078 Å for [CuCl(bheg)], and 2.181 and 2.016 Å for [Cu(bheg)]ClO_4. Therefore the strength of this O(1)–H bond seems to be stronger than those of the O(2)–H bond in this complex and other O–H bonds for [CuCl(bheg)] and [Cu(bheg)]ClO_4. The latter band overlaps with CH_2 stretching vibrations [7]. The band at 2096 cm^{-1} is assigned to the CN stretching vibration [8].

The bands at 1596 and 1386 cm^{-1} are assigned to COO^- antisymmetric and symmetric vibrations.

Powder Diffuse Reflection Spectrum and Magnetic Study

The reflection spectrum shows a broad band at about 800 nm. This wavelength is near to that of

[CuBr(bheg)(H_2O)] prepared in our laboratory [8]. This is due to the fact that both complexes are six-coordinated copper complexes.

The magnetic moment of this complex is 1.86 BM. This value shows that this complex is a normal bivalent copper complex and that there is no magnetic interaction between the copper atoms.

Supplementary Material

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

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