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Syntheses, properties, and crystal and molecular structures of bromo[*N*,*N*-bis(2-hydroxyethyl)glycinato]copper(II) and aquabromo[*N*,*N*-bis(2-hydroxyethyl)glycinato]copper(II)

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Abstract

The syntheses and characterization of bromo[*N*,*N*-bis(2-hydroxyethyl)glycinato]copper(II) (**1**) and aquabromo[*N*,*N*-bis(2-hydroxyethyl)glycinato]copper(II) (**2**) are presented. X-ray crystal structure determinations of both complexes have been carried out. Complex **1** crystallizes in the monoclinic system, space group $P2_1/n$, with $Z=4$ and unit cell parameters $a=12.910(2)$, $b=8.478(1)$ and $c=8.894(2)$ Å, and $\beta=105.11(1)$°. Complex **2** crystallizes in the orthorhombic system, space group $P2_12_12_1$, with $Z=4$ and unit cell parameters $a=8.7672(9)$, $b=15.594(3)$ and $c=7.4996(5)$ Å. In complex **1** the copper atom is in a trigonal bipyramidal geometry, while complex **2** has a distorted octahedral configuration.

Introduction

The spectral and structural properties of copper(II) complexes with *N*,*N*-bis(2-hydroxyethyl)glycine (Hbheg); [CuCl(bheg)] (**3**) [1], [Cu(bheg)]$ClO_4 \cdot H_2O$ (**4**) [2] and [Cu(bheg)NCS]$\cdot H_2O$ (**5**) [3] have been extensively explored in our laboratory.

In complexes **3** and **4** the copper atom is in a trigonal bipyramidal geometry, while in complex **5** the copper atom is at the center of a typical tetragonal bipyramidal geometry. Complexes **4** and **5** form one-dimensional polymer chains through the carboxylato group and through the isothiocyanate ion, respectively. These three complexes have three five-membered chelate rings.

In this work the structures of [CuBr(bheg)] (**1**) and [CuBr(bheg)(H_2O)] (**2**) were determined by X-ray diffraction. In addition these structures and the physical properties are compared with those of complexes **3**, **4** and **5** previously studied in our laboratory.

Experimental

Preparation of complexes

[CuBr(bheg)] (1)

Equimolar amounts of $CuBr_2$ and Hbheg were mixed in aqueous solution. Green crystals were obtained from this solution by keeping it for several days. *Anal.* Found: C, 23.43; H, 4.00; N, 4.64. Calc. for $CuBr(C_6H_{12}NO_4)$: C, 23.57; H, 3.96; N, 4.58%.

[CuBr(bheg)(H₂O)] (2)

An aqueous solution containing equimolar amounts of $CuBr_2$ and Hbheg was condensed at 60–70 °C for several hours until it became saturated. After a small quantity of water was added, it was kept in a desiccator containing ethanol for several days. Blue crystals were obtained from this solution. *Anal.* Found: C, 22.20; H, 4.35; N, 4.71. Calc. for $CuBr(C_6H_{12}NO_4)(H_2O)$: C, 22.27; H, 4.36; N, 4.33%.

X-ray measurements

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).

Structure determination

The 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 (<1.0).

[CuBr(bheg)] (1)

The structure was solved by the *R* factor method [4, 5], which is a variant of the heavy atom method.

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TABLE 1. Crystal data of [CuBr(bheg)] and [CuBr(bheg)(H_2O)]

	$CuBrC_6H_{12}NO_4$	$CuBrC_6H_{14}NO_5$
Formula weight	305.62	323.63
	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
a (Å)	12.910(2)	8.7672(9)
b (Å)	8.478(1)	15.594(3)
c (Å)	8.894(2)	7.4996(5)
β (°)	105.11(1)	
U (Å^3)	939.9(3)	1025.3(2)
Z	4	4
D_m (g cm^{-3})	2.143(7)	2.088(1)
D_x (g cm^{-3})	2.160	2.097
μ(Mo Kα) (cm^{-1})	65.2	59.9

After the position of the copper atom was obtained, the positions of all other non-hydrogen atoms were successively located by Fourier syntheses and were refined first by a block diagonal least-squares method and only in the last cycle by a full matrix least-squares method.

The positions of the hydrogen atoms were obtained by difference-Fourier syntheses. In the anisotropic temperature factors for non-hydrogen atoms, all the parameter shifts were less than one-third of the corresponding standard deviations.

The final R and R_w values for 1728 independent reflections were 0.051 and 0.058, respectively; $R=(\Sigma||F_o|-|F_c||)/\Sigma|F_o|$, $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

[CuBr(bheg)(H_2O)] (2)

The structure was solved by the direct method and refined by a full matrix least-squares method. The positions of the 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 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 for 1008 independent reflections were 0.058 and 0.065, respectively.

Physical measurements

Infrared absorption spectra, powder diffuse reflection spectra and magnetic moments were obtained by the same methods used for complexes **3**, **4** and **5**.

Results and discussion

Structure of [CuBr(bheg)]

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 atom, except the hydrogen atoms, are shown in Fig. 1.

Three five-membered *N,O*-chelate rings are formed in [CuBr(bheg)] and [CuBr(bheg)(H_2O)]. They all consist of one copper atom, one oxygen atom, one nitrogen atom and two carbon atoms.

The structure of this complex is a trigonal bipyramid. This is the same as that of [CuCl(bheg)] (3). The copper atom is surrounded by five atoms: one carboxylato oxygen atom, two hydroxyl oxygen atoms, one nitrogen atom and one bromine atom. The bromine atom and the nitrogen atom are at the apical positions. The angle Br–Cu–N is 178.8° and three coordinating oxygen atoms form a triangle around the copper atom. The copper atom is 0.23 Å above the plane (1) formed by the three ligating oxygen atoms.

The bond length of Cu–O(3)(carboxylato) (1.960 Å) is shorter than those of Cu–O(1)(hydroxyl) (2.194

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

Atom	x	y	z	B_{eq} (Å^2)
Cu	0.3337(1)	0.0786(1)	0.0225(1)	1.9
Br	0.3759(1)	0.3498(1)	0.0376(1)	2.7
O(1)	0.1584(5)	0.0907(7)	−0.0245(8)	2.7
O(2)	0.3828(5)	0.0427(7)	0.2581(7)	2.4
O(3)	0.3872(5)	0.0379(6)	−0.1608(7)	3.3
O(4)	0.4169(4)	−0.1483(7)	−0.3171(6)	2.5
N	0.3005(5)	−0.1551(6)	0.0127(7)	1.8
C(1)	0.1859(7)	−0.1795(8)	0.0112(11)	2.5
C(2)	0.1172(7)	−0.0578(10)	−0.0892(11)	2.9
C(3)	0.3754(7)	−0.2219(9)	0.1545(10)	2.5
C(4)	0.3764(8)	−0.1210(9)	0.2944(10)	2.8
C(5)	0.3236(8)	−0.2187(9)	−0.1307(10)	2.4
C(6)	0.3798(6)	−0.1013(8)	−0.2085(9)	2.2

TABLE 3. Selected bond lengths (Å) of [CuBr(bheg)] with e.s.d.s in parentheses

Cu–Br	2.359(1)	N–C(1)	1.490(11)
Cu–O(1)	2.194(7)	N–C(3)	1.487(10)
Cu–O(2)	2.048(6)	N–C(5)	1.485(12)
Cu–O(3)	1.960(7)	C(1)–C(2)	1.496(11)
Cu–N	2.024(6)	C(3)–C(4)	1.508(13)
O(1)–C(2)	1.428(10)	C(5)–C(6)	1.502(13)
O(2)–C(4)	1.432(10)	O(1)–H(O1)	0.60(10)
O(3)–C(6)	1.250(9)	O(2)–H(O2)	0.67(8)
O(4)–C(6)	1.250(10)		
O(4)···O(1)^{I}	2.667(8)	O(4)···H(O1)^{I}	2.07(11)
O(4)···O(2)^{II}	2.657(9)	O(4)···H(O2)^{II}	1.99(8)

Key to symmetry operations: $^{I}0.5-x,\ -0.5+y,\ -0.5-z$; $^{II}1-x,\ -y,\ -z$.

TABLE 4. Selected bond angles (°) of [CuBr(bheg)] with e.s.d.s in parentheses

Br–Cu–O(1)	100.2(2)	O(3)–C(6)–C(5)	118.2(8)
Br–Cu–O(2)	94.6(2)	O(4)–C(6)–C(5)	118.3(7)
Br–Cu–O(3)	95.3(2)	Cu–N–C(1)	109.6(4)
Br–Cu–N	178.8(2)	Cu–N–C(3)	104.7(4)
O(1)–Cu–O(2)	103.3(3)	Cu–N–C(5)	107.7(5)
O(1)–Cu–O(3)	114.8(3)	C(1)–N–C(3)	112.3(7)
O(2)–Cu–O(3)	138.0(3)	C(1)–N–C(5)	111.3(6)
O(1)–Cu–N	80.8(2)	C(3)–N–C(5)	111.0(6)
O(2)–Cu–N	84.5(2)	O(1)–C(2)–C(1)	105.5(6)
O(3)–Cu–N	84.8(3)	O(2)–C(4)–C(3)	110.7(7)
Cu–O(1)–C(2)	107.0(5)	N–C(1)–C(2)	110.0(7)
Cu–O(2)–C(4)	110.7(5)	N–C(3)–C(4)	110.3(7)
Cu–O(3)–C(6)	115.8(6)	N–C(5)–C(6)	112.6(6)
O(3)–C(6)–O(4)	123.5(8)		
O(4)···H(O1)^{I}–O(1)^{I}	169(18)	O(4)···H(O2)^{II}–O(2)^{II}	167(22)

Key to symmetry operations: $^{I}0.5-x,\ -0.5+y,\ -0.5-z$; $^{II}1-x,\ -y,\ -z$.

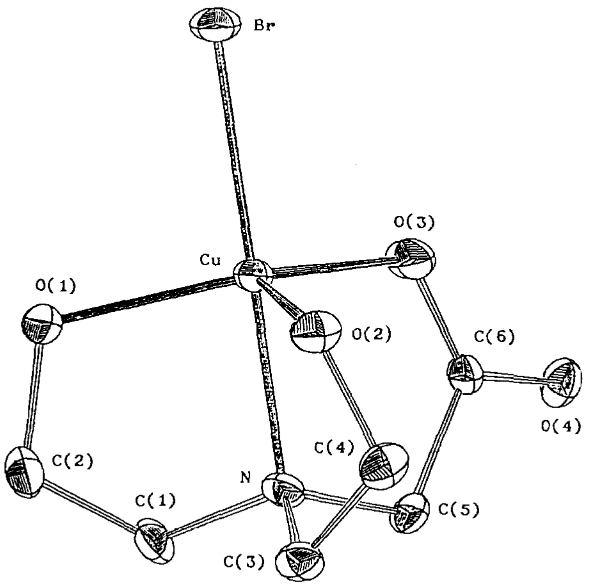

Fig. 1. Molecular structure of [CuBr(bheg)].

Å) and Cu–O(2)(hydroxyl) (2.048 Å). These values show the same trend as those of [CuCl(bheg)].

The deviations of atoms from the least-squares plane are shown in Table 5. These planes are all distorted because of the small O–Cu–N angles. Short C–C bonds and C–N bonds show the same trend as those of [CuCl(bheg)] and of the free ligand [6].

At the carboxylato functional group, the bond length of C(6)–O(3)(coordinated) is the same as that of C(6)–O(4)(non-coordinated), because O(4) forms two hydrogen bonds with the neighboring hydroxyl hydrogen.

The crystal structure of [CuBr(bheg)] is shown in Fig. 2. There are only two hydrogen bonds between the non-coordinated carboxylato oxygen atom and the hydroxyl hydrogen atom. The complexes form three-dimensional polymer chains with hydrogen bonds between each other.

TABLE 5. The deviations of atoms from the least-squares planes (Å) of [CuBr(bheg)]

Plane (1)	[O(1), O(2), O(3)]
	Cu, 0.2256
Plane (2)	[Cu, O(1), N, C(1), C(2)]
	Cu, −0.0934; O(1), 0.2934; N, −0.1755;
	C(1), 0.3146; C(2), −0.1845
Plane (3)	[Cu, O(2), N, C(3), C(4)]
	Cu, −0.0773; O(2), −0.0013; N, 0.2593;
	C(3), −0.2902; C(4), 0.1488
Plane (4)	[Cu, O(3), N, C(5), C(6)]
	Cu, 0.0273; O(3), −0.0018; N, −0.0473;
	C(5), 0.0594; C(6), −0.0355; O(4), −0.1500
Plane (5)	[O(3), O(4), C(5), C(6)]
	O(3), −0.0006; O(4), −0.0006; C(5), −0.0005
	C(6), 0.0016; Cu, −0.1525; N, −0.2358

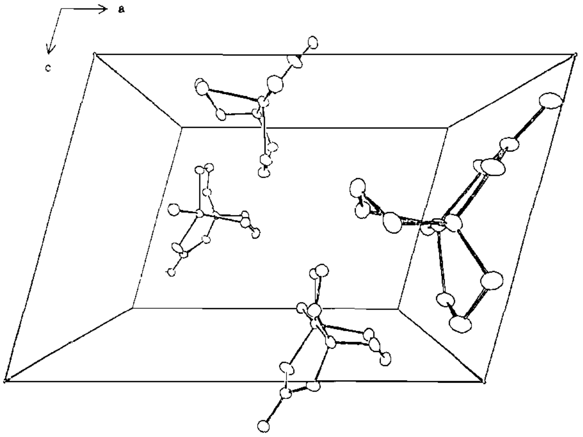

Fig. 2. Crystal structure of [CuBr(bheg)].

The only difference from [CuCl(bheg)] is that no cleavage of the crystal is found. This is because [CuCl(bheg)] has a two-dimensional polymer chain and has no intermolecular interaction parallel to the *b* axis. Although the molecular structure of [CuBr(bheg)] is almost the same as that of [CuCl(bheg)], the molecular packing of [CuBr(bheg)] is different from that of [CuCl(bheg)].

Structure of [CuBr(bheg)(H$_2$O)]

The final atomic parameters are listed in Table 6, the interatomic distances in Table 7 and the bond angles in Table 8. The deviations of atoms from the least-squares planes are shown in Table 9. Then in order to compare the results of this work with those of the previous works, the bond lengths related to the copper–ligand bonds are summarized in Table

TABLE 6. Final positional parameters and equivalent isotropic temperature factors, B_{eq} (Å^2), of [CuBr(bheg)(H_2O)] with e.s.d.s in parentheses

Atom	x	y	z	B_{eq} (Å^2)
Cu	0.2314(2)	0.1187(1)	0.2463(3)	1.8
Br	−0.0194(1)	0.0573(1)	0.2701(3)	3.5
O(1)	0.1713(13)	0.2597(7)	0.1956(14)	3.0
O(2)	0.4283(13)	−0.0116(8)	0.2368(21)	3.1
O(3)	0.2466(14)	0.1278(7)	0.5053(13)	2.5
O(4)	0.3934(12)	0.1725(8)	0.7287(17)	3.6
N	0.4464(10)	0.1740(6)	0.2501(20)	2.0
C(1)	0.4358(17)	0.2607(11)	0.1521(22)	2.1
C(2)	0.3084(19)	0.3109(9)	0.2185(25)	2.8
C(3)	0.5606(15)	0.1198(11)	0.1610(21)	2.4
C(4)	0.5758(15)	0.0255(9)	0.2359(37)	3.1
C(5)	0.4868(20)	0.1880(13)	0.4388(21)	2.9
C(6)	0.3661(16)	0.1619(10)	0.5712(20)	2.2
O(W)	0.2362(14)	0.0963(8)	−0.0101(13)	2.4

TABLE 7. Selected bond lengths (Å) of [CuBr(bheg)(H_2O)] with e.s.d.s. in parentheses

Cu–Br	2.41(1)	O(1)–C(2)	1.45(2)
Cu–O(1)	2.29(1)	O(2)–C(4)	1.44(2)
Cu–O(2)	2.67(1)	O(3)–C(6)	1.28(2)
Cu–O(3)	1.95(1)	O(4)–C(6)	1.22(2)
Cu–O(W)	1.96(1)	C(1)–C(2)	1.45(2)
Cu–N	2.07(1)	C(3)–C(4)	1.53(2)
N–C(1)	1.54(2)	C(5)–C(6)	1.51(2)
N–C(3)	1.47(2)	O(1)–H(O1)	1.2(2)
N–C(5)	1.48(2)	O(2)–H(O2)	0.7(2)
O(2)···O(W)$^{\mathrm{I}}$	2.73(2)	O(2)···H(W1)$^{\mathrm{I}}$	2.0(2)
O(4)···O(1)$^{\mathrm{II}}$	2.72(2)	O(4)···H(O1)$^{\mathrm{II}}$	1.8(2)
O(4)···O(W)$^{\mathrm{III}}$	2.67(2)	O(4)···H(W2)$^{\mathrm{III}}$	1.9(2)

Key to symmetry operations: $^{\mathrm{I}}0.5-x$, $-y$, $0.5+z$; $^{\mathrm{II}}0.5+x$, $0.5-y$, $1.0-z$; $^{\mathrm{III}}x$, y, $1.0+z$.

TABLE 8. Selected bond angles (°) of [CuBr(bheg)(H_2O)] with e.s.d.s in parentheses

Br–Cu–O(1)	100.6(3)	Cu–O(1)–C(2)	108.5(9)
Br–Cu–O(2)	106.9(3)	Cu–O(2)–C(4)	104.4(9)
Br–Cu–O(3)	91.0(4)	Cu–O(3)–C(6)	118.2(10)
Br–Cu–O(W)	91.2(4)	O(3)–C(6)–C(5)	115.8(13)
Br–Cu–N	174.8(4)	O(4)–C(6)–C(5)	117.7(13)
O(1)–Cu–O(2)	151.0(4)	Cu–N–C(1)	107.7(8)
O(1)–Cu–O(3)	96.4(4)	Cu–N–C(3)	111.9(8)
O(1)–Cu–O(W)	90.8(5)	Cu–N–C(5)	107.0(10)
O(2)–Cu–O(3)	92.2(5)	C(1)–N–C(3)	109.2(12)
O(2)–Cu–O(W)	79.8(5)	C(1)–N–C(5)	110.0(12)
O(3)–Cu–O(W)	172.0(5)	C(3)–N–C(5)	110.9(12)
O(1)–Cu–N	79.2(4)	O(1)–C(2)–C(1)	107.4(12)
O(2)–Cu–N	74.3(4)	O(2)–C(4)–C(3)	109.2(12)
O(3)–Cu–N	83.9(6)	N–C(1)–C(2)	110.9(13)
O(W)–Cu–N	93.9(6)	N–C(3)–C(4)	115.1(13)
O(3)–C(6)–O(4)	126.5(14)	N–C(5)–C(6)	115.1(14)
O(2)···H(W1)$^{\mathrm{I}}$–O(W)$^{\mathrm{I}}$	156(20)		
O(4)···H(O1)$^{\mathrm{II}}$–O(1)$^{\mathrm{II}}$	134(13)		
O(4)···H(W2)$^{\mathrm{III}}$–O(W)$^{\mathrm{III}}$	150(18)		

Key to symmetry operation: $^{\mathrm{I}}0.5-x$, $-y$, $0.5+z$; $^{\mathrm{II}}0.5+x$, $0.5-y$, $1.0-z$; $^{\mathrm{III}}x$, y, $1.0+z$.

TABLE 9. The deviations of atoms from the least-squares planes (Å) of [CuBr(bheg)(H_2O)]

Plane (1)	[Br, O(1), O(2), N]	Br, −0.0596; O(1), 0.1601; O(2), 0.1516; N, −0.2096; Cu, −0.0410
Plane (2)	[Br, O(3), O(W), N]	Br, −0.0401; O(3), 0.0653; O(W), 0.0894; N, −0.0949; Cu, −0.0532
Plane (3)	[O(1), O(2), O(3), O(W)]	O(1), −0.2627; O(2), −0.2375; O(3), 0.2210; O(W), 0.3771; Cu, 0.3268
Plane (4)	[Cu, O(1), N, C(1), C(2)]	Cu, 0.1712; O(1), 0.1405; N, −0.1932; C(1), 0.2574; C(2), −0.2914
Plane (5)	[Cu, O(2), N, C(3), C(4)]	Cu, 0.1834; O(2), 0.0947; N, −0.2698; C(3), 0.2652; C(4), −0.1939
Plane (6)	[Cu, O(3), N, C(5), C(6)]	Cu, −0.0022; O(3), 0.0114; N, −0.0030; C(5), 0.0093; C(6), −0.0150; O(4), −0.0136
Plane (7)	[O(3), O(4), C(5), C(6)]	O(3), 0.0051; O(4), 0.0040; C(5), 0.0034; C(6), −0.0122; Cu, −0.0321; N, −0.0269

10 together with powder diffuse reflection spectra and other data.

The structure of this complex is a distorted octahedron as shown in Fig. 3. The copper atom is coordinated with six atoms: one carboxylato oxygen atom, two hydroxyl oxygen atoms, one nitrogen atom, one bromine atom and one oxygen atom of the water molecule.

The copper atom is almost on the least-plane (2) formed by the bromine atom, carboxylato oxygen atom, water oxygen atom and nitrogen atom. The deviation is only 0.05 Å. These four atoms form a typical square around the copper atom.

The Cu–O(2) bond is remarkably long. The bond lengths of Cu–O(1)(hydroxyl) (2.29 Å) and Cu–O(2)(hydroxyl) (2.67 Å) are also longer than that of Cu–O(3) (carboxyl) (1.95 Å) which is slightly shorter than that for other complexes as listed in Table 10, but is almost the same as that of Cu–O(W)(water) (1.96 Å).

At the carboxylato functional group the bond lengths between C(6)–O(3)(coordinated) (1.28 Å) and C(6)–O(4)(non-coordinated) (1.22 Å) are remarkably different. This is a different trend from that observed in the other halide complexes (**1** and **3**) though the non-coordinated carboxylato oxygen atom also has two hydrogen bonds.

TABLE 10. Bond lengths (Å) related to metal–ligand bonds and physical properties

	1 CuBr(bheg)	2 CuBr(bheg)(H_2O)	3 CuCl(bheg)	4 [Cu(bheg)]$ClO_4 \cdot H_2O$	5 Cu(bheg)NCS$\cdot H_2O$
Cu–O(1)	2.194(7)	2.29(1)	2.140(4)	2.181(4)	2.37(1)
Cu–O(2)	2.048(6)	2.67(1)	2.078(3)	2.016(3)	1.98(1)
Cu–O(3)	1.960(7)	1.95(1)	1.963(3)	1.995(3)	1.98(1)
Cu–O(W)		1.96(1)			
C(6)–O(3)	1.250(9)	1.28(2)	1.252(4)	1.251(4)	1.28(2)
C(6)–O(4)	1.250(10)	1.22(2)	1.246(4)	1.265(4)	1.23(2)
Cu–N	2.024(6)	2.07(1)	2.007(3)	2.003(3)	2.01(1)
CN[a]	5	5 + 1	5	5	4 + 2
Color	green	blue	green	pale blue	blue
λ (nm)[b]	1000	770	1000	900	800
Reference	this work	this work	1	2	3

[a] CN = coordination number: for example '5 + 1' indicates that the complex has 5 usual coordination bonds and 1 weak bond. [b] Powder diffuse reflection spectra.

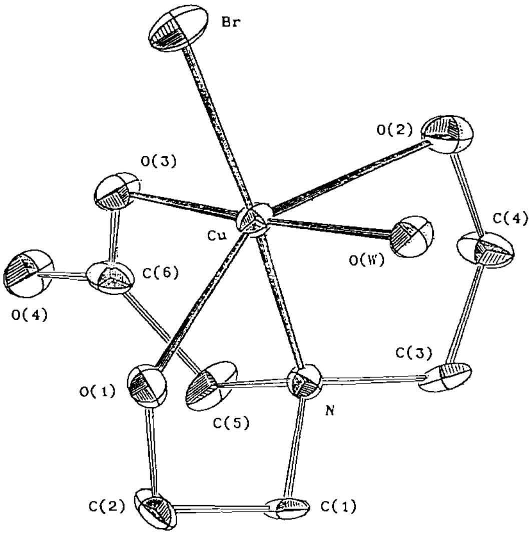

Fig. 3. Molecular structure of [CuBr(bheg)(H_2O)].

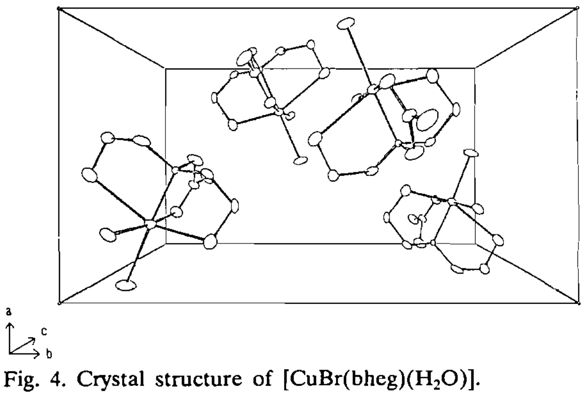

Fig. 4. Crystal structure of [CuBr(bheg)(H_2O)].

The crystal structure of [CuBr(bheg)(H_2O)] is shown in Fig. 4. Two hydrogen bonds are found between a non-coordinated oxygen atom and a water molecule and between a non-coordinated oxygen atom and a hydroxyl oxygen atom.

Infrared and far-infrared absorption spectra

The infrared spectra data related to the metal–ligand bonds are listed in Table 11. The assignments of [CuCl(bheg)] have already been carried out extensively [7]. The spectral patterns of [CuCl(bheg)] and [CuBr(bheg)] are the same. This is due to the similarity of the molecular structure of these complexes.

On coordination the band shift of the OH stretching vibration in [CuBr(bheg)(H_2O)] is smaller than those of [CuCl(bheg)] and [CuBr(bheg)]. Because the bond lengths of Cu–O(1) and Cu–O(2) are longer than the corresponding bond lengths in [CuBr(bheg)] and [CuCl(bheg)], the strength of the O–H bond in [CuBr(bheg)(H_2O)] is, therefore, stronger than that of the latter two complexes.

The frequency separation between the COO^- antisymmetric and symmetric stretching vibrations (Δ) of [CuBr(bheg)] is smaller than that of the free ligand as shown in Table 11. This is also the same trend as seen in [CuCl(bheg)]. This is due to the fact that the lengths of the C(6)–O(3) and C(6)–O(4) bonds are almost the same.

In [CuBr(bheg)(H_2O)] the frequency separation (206 cm^{-1}) is larger than those of [CuCl(bheg)] and [CuBr(bheg)], because the bond length of C(6)–O(3) (1.28 Å) is different from that of C(6)–O(4) (1.22 Å).

Below 400 cm^{-1} several new bands which cannot be observed in Hbheg appear in both bromo complexes. These are assigned to metal–ligand and metal–halogen stretching vibrations listed in Table 11. The ratio of the frequencies between (Cu–Cl) and (Cu–Br) is 0.68. This is near the empirical value (0.77–0.74) [8].

TABLE 11. Assignments of infrared absorption spectra related to metal–ligand bonds (cm^{-1})

Hbheg	CuCl(bheg)	CuBr(bheg)	CuBr(bheg)(H_2O)	Assignments
3089	3025	3000	3078	OH str.
			1678	H_2O bend.
1639	1578	1572	1599	COO^- asym. str.
1401	1406	1397	1393	COO^- sym. str.
	340	345	340	Cu–N str.
	317			Cu–Cl str.
	275	265	280, 240	Cu–O str.
		215	220	Cu–Br str.

Powder diffuse reflection and electronic spectra

[CuBr(bheg)]

The reflection spectrum shows a broad band at about 1000 nm. This wavelength is the same as that of [CuCl(bheg)] as shown in Table 10. This is due to the fact that the molecular structures of [CuCl(bheg)] and [CuBr(bheg)] are the same.

The electronic spectrum of the aqueous solution shows a broad band at about 760 nm. This result shows that the structure of the complex changes in aqueous solution.

[CuBr(bheg)(H_2O)]

The reflection spectrum shows a broad band at about 770 nm. This is different from the spectra of [CuCl(bheg)] [1] and [CuBr(bheg)]. This is due to the fact that the geometry of this complex is different from those of the above halogeno complexes.

The electronic spectrum of the aqueous solution shows a broad band at about 760 nm. This value shows that the molecular structure in aqueous solution is not so different from that in the crystalline state.

Magnetic moment

The values of magnetic moment for complexes **1** (1.88 BM) and **2** (1.77 BM) correspond to that of a normal bivalent copper complex. So there is no magnetic interaction between the copper atoms.

Supplementary material

Observed and calculated structure factors, anisotropic thermal parameters, and hydrogen atom coordinates are available from the authors on request.

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