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Short Communications

Benzotriazole Complexes. V. The Crystal Structure of Catena-μ-aqua-bis(μ-benzotriazolato)copper(II)

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The present structure analysis is part of an investigation of benzotriazole complexes.[1–4] The benzotriazolate ion is henceforth referred to as BTA.

Blue crystals of $[Cu(H_2O)(C_6H_4N_3)_2]$ were precipitated by mixing 3×10^{-4} mol cupric chloride dihydrate in 20 ml of 7 M ammonia and 1.5×10^{-3} mol of benzotriazole in 15 ml of 7 M ammonia. The crystals were very small needles, and several attempts to grow larger crystals failed. Therefore the dimensions of the crystal used were 0.02×0.02×0.12 mm. The possible space groups were established by Weissenberg photographs using Cu-radiation. Three-dimensional data were measured on a four-circle diffractometer (CAD-4F) using monochromated Cu-radiation and ω-scan technique. Because of the small crystal size only reflections with $\theta\leq50$

Table 1. Crystal Data.

M	299.8
μ(Cu$K\alpha$) (cm^{-1})	24.6
Crystal system	monoclinic
V (Å^3)	2513.1
a (Å)	21.533(5)
b (Å)	6.862(3)
c (Å)	17.059(6)
β (°)	94.44(2)
Space group	$I\,2/c$
D_c (g/cm^3)	1.68
Z	8
Total number of reflections	1351
Number of independent observations $[I\geq2\sigma(I)]$	828
$R=\Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.079
$R_w=\left[\frac{\Sigma w(\|F_o\|-\|F_c\|)^2}{\Sigma w\|F_o\|^2}\right]^{\frac{1}{2}}$	0.094

Table 2. Atomic coordinates ×10^4. The estimated standard deviations ×10^4 are given in parentheses. The values for the hydrogen atoms are multiplied by 10^3. The isotropic temperature factors for the nonhydrogen atoms are estimated from the anisotropic values.[6]

Atom	x	y	z	B_{eq}
Cu	2428(1)	2126(4)	29(2)	3.4
O	2217(5)	–372(19)	–1010(7)	3.4
BTA1				
N1	2009(6)	425(27)	781(8)	2.2
N2	2127(6)	–1432(22)	798(10)	2.3
N3	1871(6)	–2372(25)	1375(9)	2.8
C4	1574(7)	–893(29)	1748(11)	2.0
C5	1661(8)	916(26)	1394(11)	2.2
C6	1395(8)	2619(32)	1648(11)	2.7
C7	1049(8)	2388(37)	2311(12)	3.1
C8	953(9)	605(44)	2641(13)	3.6
C9	1213(10)	–1045(35)	2427(14)	3.4
H1	148(8)	401(27)	134(10)	3.9
H2	86(9)	354(29)	239(11)	3.9
H3	78(9)	34(32)	297(11)	3.9
H4	127(9)	–233(29)	257(12)	3.9
BTA 2				
N1	1678(7)	3827(25)	–234(9)	2.3
N2	1770(6)	5703(29)	–329(8)	2.5
N3	1271(7)	6651(23)	–603(9)	2.6
C4	827(8)	5250(30)	–697(10)	1.9
C5	1058(8)	3471(30)	–482(10)	2.1
C6	718(9)	1789(34)	–500(14)	2.9
C7	118(9)	1936(4)	–789(14)	3.7
C8	–133(10)	3718(42)	–1019(16)	4.1
C9	203(10)	5345(39)	–1005(13)	3.3
H1	94(10)	101(33)	–38(14)	3.9
H2	–5(10)	104(30)	–102(12)	3.9
H3	–53(9)	371(29)	–108(11)	3.9
H4	11(10)	623(31)	–118(14)	3.9

0302-4377/84 $2.50

Table 3. Bond distances (Å) and bond angles (°) with estimated standard deviations in the copper coordination sphere. The figures in parentheses refer to the number of the BTA ligands. Superscript refer to atoms in the following positions: a $\frac{1}{2}-x, \frac{1}{2}+y, -z$; b $\frac{1}{2}-x\ -\frac{1}{2}+y, -z$.

Atoms	Distance or angle
Cu–N1(1)	2.00(2)
Cu–N1(2)	2.01(2)
Cu–N2(1[a])	2.02(2)
Cu–N2(2[b])	2.02(1)
Cu–O	2.48(1)
Cu–O[a]	2.48(1)
N1(1)–Cu–N1(2)	95.0(6)
N1(1)–Cu–N2(2[b])	88.5(6)
N1(1)–Cu–O	89.3(5)
N1(1)–Cu–O[a]	95.9(5)
N1(2)–Cu–N2(1[a])	88.6(6)
N1(2)–Cu–O	98.1(5)
N1(2)–Cu–O[a]	87.1(5)
N2(1[a])–Cu–N2(2[b])	88.3(6)
N2(1[a])–Cu–O	84.9(5)
N2(1[a])–Cu–O[a]	89.6(5)
N2(2[b])–Cu–O	87.3(5)
N2(2[b])–Cu–O[a]	87.1(5)

were measured. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

The structure was solved by Patterson technique.[5] The references to atomic scattering factors and the refinement technique are as given in Ref. 1. The hydrogen atoms in the water molecule were not located, and the temperature factors of the remaining hydrogen atoms were kept invariant during refinement. Crystal data and *R*-values are listed in Table 1. The final positional parameters with e.s.d.'s are listed in Table 2. The labelling of the atoms in the benzotriazolate groups are as in Ref. 1. Lists of thermal parameters as well as lists of observed and calculated structure factors may be obtained from the authors on request.

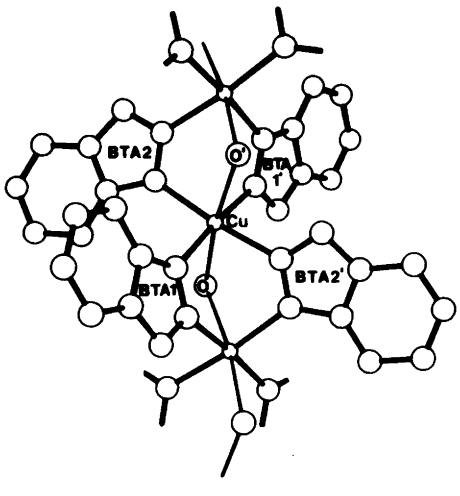

Fig. 1. The coordination around the Cu-atoms.[9]

Table 4. Bond distances (Å) and bond angles (°) with estimated standard deviations in the BTA ligands.

Atoms	BTA 1 Distance or angle	BTA 2 Distance or angle
N1–N2	1.30(2)	1.31(3)
N2–N3	1.33(2)	1.31(2)
N3–C4	1.38(2)	1.36(2)
C4–C5	1.40(3)	1.36(3)
C5–N1	1.38(2)	1.39(2)
C5–C6	1.39(3)	1.37(3)
C6–C7	1.41(3)	1.35(3)
C7–C8	1.37(4)	1.38(4)
C8–C9	1.33(4)	1.33(4)
C9–C4	1.45(3)	1.41(3)
C6–H1	1.11(18)	0.73(23)
C7–H2	0.90(20)	0.80(21)
C8–H3	0.73(20)	0.86(19)
C9–H4	0.92(20)	0.70(22)
C5–N1–N2	109.8(1.5)	106.5(1.4)
N1–N2–N3	113.6(1.5)	113.8(1.4)
N2–N3–C4	102.5(1.5)	104.0(1.5)
N3–C4–C5	111.8(1.6)	111.3(1.5)
C4–C5–N1	102.1(1.6)	104.4(1.6)
C4–C5–C6	122.8(1.8)	124.6(1.7)
C5–C6–C7	114.3(1.9)	116.1(2.1)
C6–C7–C8	122.5(2.2)	120.8(2.3)
C7–C8–C9	124.6(2.1)	122.6(2.0)
C8–C9–C4	115.0(2.1)	118.1(2.3)
C9–C4–C5	120.5(1.8)	117.6(1.9)

Description and discussion of the structure. Bond lengths and bond angles with e.s.d.'s are listed in Tables 3 and 4. The complex is polymeric. The four Cu atoms with $y \sim \frac{1}{4}$ are linked to the remaining Cu atoms in the *y*-direction, $(\frac{1}{2}-x, \frac{1}{2}+y, -z)$, by two bridging BTA groups (Fig. 1). The four bridging nitrogen atoms are nearly coplanar, the deviations from the least-squares plane being less than 0.1 Å. The Cu atom is lying in the plane. The coordination polyhedron around Cu is a distorted tetragonal bipyramid, with apices of the elongated axis

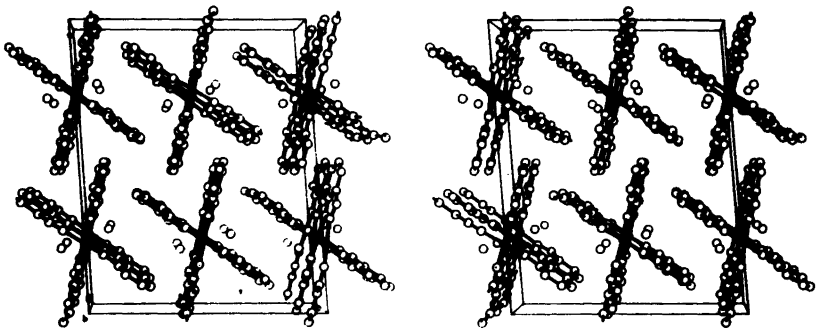

Fig. 2. Stereoview along the *b*-axis of the structure.

occupied by water molecules. The polyhedra are linked together by sharing these apices. The Cu–O–Cu^a angle is 88.1°. The angle between the normal of the equatorial plane and the normals of the planes through the BTA ligands are 44.3° and 45.9°, respectively.

The Cu–O distance of 2.48(1) Å falls within the range of 2.31–2.64 Å found in other tetragonal bipyramidal copper complexes.[7,8] There are no Cu–Cu bonds in the chains. The Cu–Cu distance is 3.447(4) Å, which is in agreement with the values of 3.520(2) Å and 3.448(3) Å found in the two dimers of $[Cu(BTAH)_2Cl_2]_2 \cdot H_2O$.[1] The BTA ligands are nearly planar, the deviations of the atoms from the least-squares plane through them being less than 0.04 Å. Because of the large standard deviations on bond distances and bond angles of the BTA ligands, a discussion of these is omitted.

The packing of the structure is shown in Fig. 2. The planes of the BTA ligands are almost perpendicular to the *ac*-plane, whereas the angles between the *ab*-plane and the BTA1 and BTA2 planes are 52.6 and 21.9°, respectively.

The hydrogen-bonding distances (2.95–3.19 Å) involving the water molecule are directed along the edges of the copper coordination polyhedron. The shortest distance (2.95 Å) is found to N3[BTA1($\frac{1}{2}-x$, $\frac{1}{2}+y$, $-z$)].

The shortest distance [3.44(2) Å] from an O atom to a BTA ligand of another chain is found to C9[BTA1(x, $-y$, $\frac{1}{2}-z$)]. Between BTA2 ligands of different chains the shortest non-bonded distance is the C4–C8($-x$, $1-y$, $-z$) distance of 3.46(3) Å. Between the BTA1 ligands of different chains all distances exceed 4 Å. The shortest distance, 3.56(3) Å, between BTA1 and BTA2 is found from C8[BTA1] to N3[BTA2(x, $1-y$, $\frac{1}{2}+z$)].

The present structure shows that the BTA ligands are arranged in such a way that the chain of Cu atoms is well covered. A similar feature was found in $[Cu(BTAH)_2Cl]_2 \cdot H_2O$.[1]

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