

The Crystal Structure of Dibromo{1-[2-pyridyl(ethoxy)methylamino]-2-(2-pyridylmethyleamino)ethane} Copper(II) Monohydrate

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Pajunen, Aarne and Pajunen, Seija. 1986. The Crystal Structure of Dibromo{1-[2-pyridyl(ethoxy)methylamino]-2-(2-pyridylmethyleamino)ethane}-Copper(II) Monohydrate. *Acta Chem. Scand. A40*: 190–193.

The crystal structure of the title compound was determined by single crystal X-ray diffraction methods. $[\text{CuBr}_2(\text{C}_{16}\text{H}_{20}\text{N}_4\text{O})] \cdot \text{H}_2\text{O}$ crystallizes in space group $\text{P2}_1/\text{n}$ with $a = 10.682(4)$, $b = 12.353(5)$, $c = 14.246(7)$ Å, $\beta = 102.91(6)^\circ$. The structure was refined to $R = 0.061$ for 2572 observed reflections. The crystal structure consists of six-coordinate complexes and water molecules. The coordination sphere of the copper atom is defined by the four N atoms of the ligand molecule in a planar arrangement and two bromide ions in the axial positions. The three five-membered rings formed by the coordination are fused and have different conformations.

Metal complexes formed by Cu^{II} and Schiff bases derived from ethylenediamine and pyridine-2-aldehyde were first described by Busch and Bailar¹ and Goodwin and Lions². They prepared [1,2-bis(2-pyridylmethyleamino)ethane]copper(II) perchlorate in the form of blue-grey crystals and the corresponding chloride as green powder. In the latter case, blue crystals formed upon standing as well. On the basis of IR-spectra, the authors proposed that the blue crystals were the hydrated form of the complex.

To study the crystal structures of compounds containing fused chelate rings, we prepared complexes from CuBr_2 and Schiff bases containing ethylenediamine, 1,3-propanediamine or 1,4-butanediamine as the amino part and pyridine-2-aldehyde as the carbonyl part. The crystal structures of the complexes formed with the two latter Schiff bases have been reported.³ This paper describes the preparation and crystal structure determination of the title compound, which was unexpectedly obtained in an attempt to prepare

dibromo[1,2-bis(2-pyridyl-methyleamino)ethane]copper(II).⁴

Experimental

Preparation. 0.12 mol pyridine-2-aldehyde in 50 ml of ethanol was mixed with 0.06 mol ethylenediamine in 50 ml of ethanol, whereupon considerable heat was evolved. 0.06 mol CuBr_2 in 50 ml methanol was then added. The resulting green mixture was gently warmed and the blue crystal product was obtained by cooling the solution. The crystals were stable in air and were of a size suitable for X-ray work.

Crystallographic examination. A crystal of approximate dimensions $0.1 \times 0.2 \times 0.5$ mm³ was selected for X-ray analysis. The unit cell parameters and the rotation matrix were determined by a least-squares refinement of 14 centred reflections measured at ambient temperature on a Nicolet P3 diffractometer. Intensity data were collected ($3^\circ < 2\theta < 50^\circ$) in the ω -scan mode using graphite monochromated $\text{MoK}\alpha$ radiation, with variable scan speed of 1.5–29.3°/min. Of the

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3238 independent reflections measured, 2572 had $I > 2\sigma(I)$ and were used for subsequent calculations. Intensities were corrected for Lorentz and polarization effects and an empirical correction was made for the effects of absorption.⁵

Crystal data. $[\text{CuBr}_2(\text{C}_{16}\text{H}_{20}\text{N}_4\text{O})] \cdot \text{H}_2\text{O}$, $M_r = 525.8$, monoclinic, $a = 10.682(4)$, $b = 12.353(5)$, $c = 14.246(7)$ Å, $\beta = 102.91(6)^\circ$, $V = 1832.3$ Å³, $D_m = 1.86$, $D_x = 1.91$ g cm⁻³, $Z = 4$, $F(000) = 1044$, $\mu(\text{MoK}\alpha) = 58.8$ cm⁻¹, space group $P2_1/n$.

Structure determination and refinement. The structure was solved by heavy-atom and Fourier methods and refined by full-matrix least-squares. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = (40.0 + |F_o| + 0.01|F_o|^2)^{-1}$. The structure was refined first isotropically and then with anisotropic temperature factors for all nonhydrogen

Table 1. Fractional atomic coordinates ($\times 10^4$) and U_{eq} ($\times 10^2$) for the nonhydrogen atoms, with e.s.d.'s in parentheses.

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Atom	x	y	z	U_{eq}
Br(1)	-103(1)		8847(1)	2493(1) 5.87(7)
Br(2)	721(1)		4119(1)	2276(1) 4.46(5)
Cu	524(1)		6696(1)	2362(1) 3.93(6)
(1)	4012(9)		6482(11)	4246(8) 9.7(7)
O(2)	2745(11)		1856(10)	6503(9) 10.5(8)
N(1)	-1279(7)		6327(6)	1547(5) 3.7(4)
N(2)	866(7)		6743(7)	1078(5) 3.8(4)
N(3)	2471(7)		6797(6)	2782(6) 3.9(4)
N(4)	661(8)		6451(7)	3765(5) 3.9(4)
C(1)	-2383(9)		6129(9)	1794(7) 4.4(5)
C(2)	-3531(11)		5928(9)	1116(9) 5.1(6)
C(3)	-3495(11)		5879(9)	180(9) 5.5(6)
C(4)	-2363(11)		6057(10)	-116(7) 5.0(2)
C(5)	-1274(9)		6284(7)	579(7) 3.6(5)
C(6)	-30(9)		6494(8)	370(7) 4.1(5)
C(7)	2195(11)		6978(10)	1047(7) 5.3(6)
C(8)	3024(10)		6486(9)	1959(8) 4.8(6)
C(9)	2876(10)		6123(9)	3645(9) 5.4(7)
C(10)	1862(10)		6243(8)	4250(7) 4.5(5)
C(11)	2173(12)		6123(9)	5247(8) 5.7(6)
C(12)	1210(17)		6191(10)	5740(7) 7.0(8)
C(13)	-18(14)		6409(10)	5259(8) 6.2(7)
C(14)	-239(11)		6546(9)	4271(7) 4.9(6)
C(15)	5103(39)		5752(28)	4340(28) 24.1(40)
C(16)	6203(26)		6068(21)	3886(19) 14.6(21)

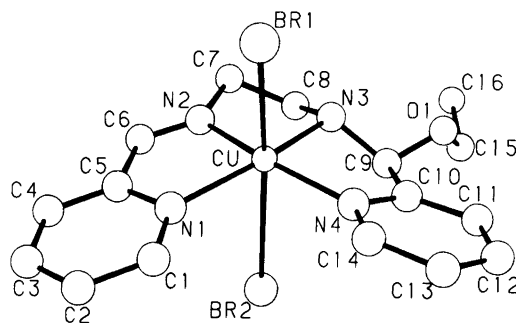


Fig. 1. Perspective view of the complex. H atoms have been omitted.

atoms. The large temperature factors provide evidence for disorder in atoms C(15), C(16) and O(1), but discrete sites for alternative conformations could not be found on difference maps. Hydrogen atoms, except those bound to C(15), C(16) and to the water molecule, were included at calculated positions and they were given a common isotropic thermal parameter $U = 0.06$ Å². The final R-value was 0.061 and the weighted discrepancy factor R_w was 0.090. The final difference map was featureless. The scattering factors used were those of Cromer and Mann⁶ except for hydrogen, where values of Stewart et al.⁷ were employed. The corrections for anomalous dispersion for Cu and Br were taken from International Tables for X-ray Crystallography⁸. The computer programs used were the XRAY76 system⁹ for solution and refinement of the structure and PLUTO¹⁰ for drawing. Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1. A list of observed and calculated structure factors as well as anisotropic thermal parameters may be obtained from the authors.

Discussion

The crystal structure is composed of discrete complex molecules and water molecules. The bond lengths and bond angles are listed in Table 2. A perspective view of the complex with numbering scheme is shown in Fig. 1. The title compound is formed by addition of one ethanol molecule to one $-\text{C}=\text{N}-$ double bond of dibromo[1,2-bis(2-pyridylmethylamino)ethane]copper(II). This will decrease the strain in the system of three fused five-membered rings.^{11,12}

Table 2. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses.

Cu—Br(1)	2.757(2)	Cu—Br(2)	3.195(2)
Cu—N(1)	2.065(7)	Cu—N(4)	2.035(7)
Cu—N(2)	1.945(8)	Cu—N(3)	1.994(8)
N(1)—C(1)	1.33(1)	N(4)—C(14)	1.33(2)
N(1)—C(5)	1.38(1)	N(4)—C(10)	1.34(1)
C(1)—C(2)	1.40(1)	C(13)—C(14)	1.38(2)
C(2)—C(3)	1.34(2)	C(12)—C(13)	1.36(2)
C(3)—C(4)	1.38(2)	C(11)—C(12)	1.37(2)
C(4)—C(5)	1.38(1)	C(10)—C(11)	1.39(1)
C(5)—C(6)	1.45(1)	C(9)—C(10)	1.53(2)
N(2)—C(6)	1.26(1)	N(3)—C(9)	1.47(1)
N(2)—C(7)	1.46(1)	N(3)—C(8)	1.48(2)
C(7)—C(8)	1.52(1)	C(15)—C(16)	1.51(5)
O(1)—C(9)	1.39(1)	O(1)—C(15)	1.46(4)
Br(1)—Cu—N(1)	92.3(2)	Br(2)—Cu—N(1)	79.6(2)
Br(1)—Cu—N(2)	97.7(3)	Br(2)—Cu—N(2)	88.0(3)
Br(1)—Cu—N(3)	99.7(2)	Br(2)—Cu—N(3)	90.0(2)
N(1)—Cu—N(2)	79.9(3)	N(3)—Cu—N(4)	82.7(3)
N(1)—Cu—N(4)	112.4(3)	N(2)—Cu—N(3)	83.1(3)
Cu—N(1)—C(1)	131.6(6)	Cu—N(4)—C(14)	129.1(6)
Cu—N(1)—C(5)	111.0(6)	Cu—N(4)—C(10)	113.2(7)
Cu—N(2)—C(6)	118.4(7)	Cu—N(3)—C(9)	107.4(6)
Cu—N(2)—C(7)	115.0(5)	Cu—N(3)—C(8)	108.3(6)
C(1)—N(1)—C(5)	117(1)	C(10)—N(4)—C(14)	118(1)
N(1)—C(1)—C(2)	123(1)	N(4)—C(14)—C(13)	124(1)
C(1)—C(2)—C(3)	118(1)	C(12)—C(13)—C(14)	117(1)
C(2)—C(3)—C(4)	121(1)	C(11)—C(12)—C(13)	120(1)
C(3)—C(4)—C(5)	118(1)	C(10)—C(11)—C(12)	119(1)
N(1)—C(5)—C(6)	114(1)	N(4)—C(10)—C(9)	116(1)
N(1)—C(5)—C(4)	122(1)	N(4)—C(10)—C(11)	122(1)
C(4)—C(5)—C(6)	124(1)	C(9)—C(10)—C(11)	122(1)
N(2)—C(6)—C(5)	116(1)	N(3)—C(9)—C(10)	108(1)
C(6)—N(2)—C(7)	126(1)	C(8)—N(3)—C(9)	115(1)
N(2)—C(7)—C(8)	106(1)	N(3)—C(8)—C(7)	108(1)
O(1)—C(9)—N(3)	113(1)	O(1)—C(9)—C(10)	105(1)
C(9)—O(1)—C(15)	115(2)	O(1)—C(15)—C(16)	119(3)

Coordination around Cu is tetragonally distorted octahedral. The Cu atom is surrounded by an approximately planar arrangement of the four coordinating nitrogen atoms. The copper atom lies 0.179(4) Å out of the plane of the four atoms in the direction of Br(1). Two bromide ions complete the coordination at longer distances of 2.757(2) and 3.195(2) Å. All three five-membered rings formed in the coordination have different conformations. Deviations from planarity have been analyzed by calculating least-squares planes. The ring containing Cu, N(1), C(5), C(6) and N(2) is almost planar, the maximum deviation

from the least-squares plane being 0.027(8) Å for N(2). The methylene bridge adopts an unsymmetrical gauche conformation with one carbon atom, C(7), 0.196(14) Å above and the other, C(8), 0.443(24) Å below the Cu, N(2), N(3) plane. The third ring, containing Cu, N(3) and N(4) is in envelope conformation, N(3) deviates 0.574(12) Å from the best plane through Cu, N(4), C(9) and C(10). All bite angles are less than 90°, ranging from 79.8° to 83.1°. The dihedral angle between planes Cu, N(1), N(2) and Cu, N(3), N(4) is 13.4(4)°.

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Received September 10, 1985.