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A Carbinolamine Bonded to Copper(II): Crystal and Molecular Structure (X-ray Analysis) of Dibromo-[2-picolyl-(2-pyridylmethanol)methylamine] copper(II) Monohydrate

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Reaction of 2-picolylmethylamine with $CuBr_2$ in water in an open vessel gives, together with other products, green crystals of the title compound, the structure of which has been determined by a three-dimensional X-ray structural analysis. Crystals were monoclinic with a = *8.38(1),* b = *27.60(3),* c = *7.69(1) Å, and β = 114.6(1)°, space group* $P2_1/c$ *and Z = 4. The structure was solved by conventional Patterson and Fourier techniques, and was refined anisotropically by least-squares methods, using 1098 unique reflections to a final R of 0.070. Data were obtained photographically, with intensities determined on an integrating microdensitometer. The analysis shows each copper atom to be five-coordinate* $[Cu(N_3)Br_2]$, *intermediate in structure between the square pyramidal and trigonal bipyramidal extremes. The metal is bonded to a terdentate ligand which is an unusual carbinolamine formed by the condensation of one mol of 2-picolylmethylamine with a mol of pyridine-2-aldehyde, formed by oxidative de-amination of the amine. Bond lengths in the co-ordination polyhedron are: Cu–Br(1) 2.598(3), Cu–Br(2) 2.436(3), Cu–N(pyridyl) 1.98(1) (av), and Cu–N (tertiary amine) 2.07(1) Å. The water molecule is hydrogen-bonded to the alcohol group of the* $[N_3]$ *ligand, and joins adjacent molecules through H-bonds to their Br(1) s.*

Introduction

During an extensive study [1] of the copper(II) compounds of a variety of substituted picolylamines, we have found a number of different compounds that appear to represent ligand reaction products. One such is the green species which crystallised, together with the blue–violet dibromobis(-2-picolylmethylamine)copper(II), from aqueous solutions of 2-picolylmethylamine (2 mol) and copper(II) bromide (1 mol) when such solutions were set aside in the air.

Experimental

Green leaflets from water were elongated along the *a* axis. Difficulty was experienced in obtaining a suitable crystal, and the one used was a fragment, which had ω-dependent spot shapes, made up of at least four distinct peaks in the Weissenberg photographs. Sampling has relied on visual inspection of the bulk sample. Cell dimensions were from Weissenberg photographs, calculated by a least-squares fit to spot position.

Crystal Data

$C_{13}H_{15}Br_2CuN_3O \cdot H_2O$, M = 470.6, Monoclinic, *a* = 8.38(1), *b* = 27.60(3), *c* = 7.69(1) Å, β = 114.6(1)°, U = 1617.2 Å^3, D_m = 1.91 g cm^{-3} (flotation), Z = 4, D_c = 1.93 g cm^{-3}, F(000) = 924. Space group $P2_1/c$ (C_{2h}^5, No. 14) from systematic absences. Cu-K$_\alpha$ radiation, λ = 1.5418 Å, μ(Cu-K$_\alpha$) = 78.1 cm^{-1}.

Data were collected photographically on a Nonius Weissenberg camera, with multiple film packs, for layers *0kl* → *7kl*. Intensities were determined with an Optronics P-100 Photoscan microdensitometer, producing 2393 observable intensities, with agreement between symmetry equivalent reflections around 4 → 6%. These gave 1098 unique reflections with a predicted R of 0.054 (based on F).

Corrections were applied for Lorentz and polarisation factors, but not for absorption.

The structure was solved by Patterson and Fourier methods, using the SHELX system of programmes. Refinement by full-matrix least-squares methods reduced R to 0.070 for 199 refined parameters. These include: positional and anisotropic parameters for all non-hydrogen atoms; an overall scale factor; inter-

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TABLE I. (a) The Experimental Atomic Positions (× 10^4) and the Anisotropic Thermal Parameters (× 10^4) for the Non-hydrogen Atoms. Anisotropic temperature factors are of the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12} + ...)]$. Estimated standard deviations are given in parentheses. (b) The Calculated Positions for the Hydrogen Atoms (× 10^3). All were given a fixed U of 0.07.

	x/a	*y/b*	*z/c*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu	2649(4)	1090(1)	3431(3)	469(11)	593(16)	340(15)	−64(13)	150(14)	−96(13)
Br(1)	698(3)	1773(1)	1255(4)	731(11)	712(15)	775(17)	338(12)	332(14)	204(12)
Br(2)	3013(3)	418(1)	1573(3)	574(10)	582(13)	551(13)	−146(10)	254(11)	−32(11)
O(1)	5345(19)	1832(5)	8478(21)	729(49)	918(96)	541(90)	−171(82)	233(80)	−204(86)
O(2)	2799(23)	2688(7)	4083(29)	1196(78)	1068(112)	1323(150)	343(113)	882(126)	42(107)
N(1)	4847(19)	1443(5)	3884(19)	422(43)	582(84)	261(82)	−75(70)	32(75)	−108(77)
N(2)	3600(19)	1210(5)	6343(19)	342(39)	338(70)	345(74)	−64(61)	119(65)	23(67)
N(3)	641(19)	801(6)	3805(20)	445(46)	691(85)	199(83)	74(70)	101(80)	42(78)
C(1)	5620(27)	1458(7)	2633(28)	550(61)	529(103)	571(125)	12(93)	259(111)	−54(98)
C(2)	7084(26)	1738(8)	3061(27)	562(62)	819(129)	305(107)	152(99)	120(98)	169(118)
C(3)	7790(29)	1974(7)	4770(33)	647(76)	498(101)	795(156)	185(101)	399(131)	−195(99)
C(4)	7053(26)	1979(7)	6004(33)	597(69)	362(99)	831(143)	229(99)	319(123)	16(96)
C(5)	5498(23)	1690(6)	5488(26)	375(49)	235(86)	514(107)	112(84)	−14(93)	49(81)
C(6)	4395(25)	1688(6)	6613(26)	443(56)	510(108)	374(111)	−45(88)	133(96)	105(95)
C(7)	4864(25)	815(7)	7355(27)	561(62)	526(98)	595(126)	−105(93)	355(107)	103(97)
C(8)	2026(29)	1205(8)	6842(31)	665(73)	731(126)	599(136)	−103(109)	326(122)	−126(113)
C(9)	657(25)	896(6)	5546(26)	410(54)	383(101)	437(114)	−28(85)	−186(106)	−99(91)
C(10)	−690(25)	682(6)	5991(30)	549(68)	386(97)	711(132)	189(97)	445(116)	288(95)
C(11)	−1995(28)	423(8)	4684(28)	575(61)	719(124)	431(117)	−53(108)	79(107)	−239(115)
C(12)	−2074(28)	369(6)	2875(34)	559(67)	171(87)	948(149)	51(98)	210(128)	20(87)
C(13)	−663(24)	550(6)	2460(27)	414(53)	426(94)	401(108)	51(86)	−22(102)	122(90)
H(1)	511(3)	124(1)	134(3)		$H(7^{11})$	584(3)	79(1)	678(3)	
H(2)	773(3)	175(1)	210(3)		H(8)	245(3)	107(1)	828(3)	
H(3)	893(3)	220(1)	509(3)		$H(8^1)$	153(3)	157(1)	676(3)	
H(4)	756(3)	218(1)	732(3)		H(10)	−63(3)	74(1)	741(3)	
H(6)	334(3)	195(1)	603(3)		H(11)	−300(3)	27(1)	505(3)	
H(7)	417(3)	48(1)	714(3)		H(12)	−317(3)	18(1)	179(3)	
$H(7^1)$	550(3)	89(1)	887(3)		H(13)	−64(2)	49(1)	108(3)	

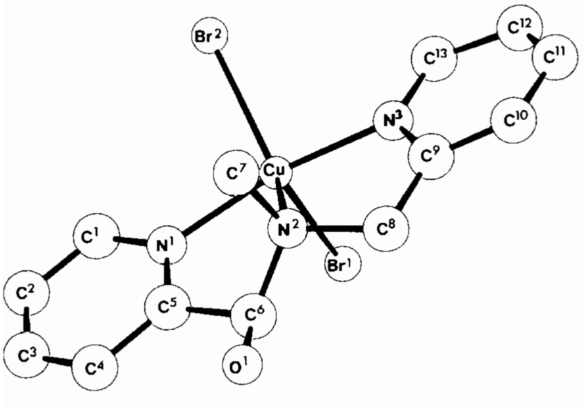


Figure 1. The molecule and the atom-labelling scheme. Hydrogen atoms attached to carbons are given the same numbers as the carbon atoms.

layer scale factors; and weighting scheme and extinction parameters. Weights were proportional to $1/(\sigma^2F + gF^2)$ where g refined to 0.014315. The values of U_{11} for each atom were automatically reset to the mean of U_{22} and U_{33} because of the one-axis data set. Hydrogen atoms bonded to carbon or nitrogen (but not oxygen) were included, but not refined, in calculated positions 1.08 Å from the appropriate atom, and U was fixed at 0.07.

The final difference Fourier has a highest peak of 1.1 e$Å^{-3}$ near Br, 0.6 e$Å^{-3}$ in the regions away from the heavy atoms, and a lowest peak of −1.0 e$Å^{-3}$.

Scattering factors were taken from ref. 2 and anomalous dispersion corrections from ref. 3.

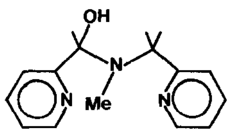
Fractional co-ordinates for atomic positions, with estimated standard deviations, together with the calculated positions of the hydrogen atoms and the thermal parameters are given in Table I.

Results and Discussion

The asymmetric unit consists of monomeric five-co-ordinate copper(II) polyhedra (Fig. 1) and a water molecule. In the former, the metal atom is bonded to two bromine atoms and a terdentate [N_3] ligand I, the –OH substituent of which is hydrogen-bonded to the water molecule. The latter

TABLE II. Bond Lengths (A) and Angles (°), with Estimated Standard Deviations in Parentheses.

(a) The co-ordination sphere of the metal			
(i) Bond lengths			
Cu–Br(1)	2.598(3)	Cu–N(1)	1.983(14)
Cu–Br(2)	2.436(3)	Cu–N(2)	2.067(13)
		Cu–N(3)	1.988(14)
(ii) Bond Angles			
Br(1)–Cu–Br(2)	111.9(1)	Br(2)–Cu–N(2)	132.2(4)
Br(1)–Cu–N(1)	92.6(4)	Br(2)–Cu–N(3)	95.7(4)
Br(1)–Cu–N(2)	115.9(4)	N(1)–Cu–N(2)	79.6(5)
Br(1)–Cu–N(3)	92.4(4)	N(1)–Cu–N(3)	162.2(5)
Br(2)–Cu–N(1)	98.2(4)	N(2)–Cu–N(3)	82.9(5)
(b) The [N_3] ligand			
(i) Bond lengths			
N(1)–C(1)	1.37(2)	C(7)–N(2)	1.49(2)
N(1)–C(5)	1.31(2)	C(8)–N(2)	1.52(2)
C(1)–C(2)	1.37(2)	C(8)–C(9)	1.44(2)
C(2)–C(3)	1.36(3)	C(9)–C(10)	1.44(2)
C(3)–C(4)	1.33(2)	C(9)–N(3)	1.36(2)
C(4)–C(5)	1.44(2)	C(10)–C(11)	1.34(2)
C(5)–C(6)	1.51(2)	C(11)–C(12)	1.37(3)
C(6)–O(1)	1.38(2)	C(12)–C(13)	1.44(3)
C(6)–N(2)	1.45(2)	C(13)–N(3)	1.34(2)
(ii) Bond angles			
C(1)–N(1)–Cu	125(1)	C(7)–N(2)–C(6)	114(1)
C(5)–N(1)–Cu	114(1)	C(8)–N(2)–Cu	107(1)
C(5)–N(1)–C(1)	121(1)	C(8)–N(2)–C(6)	112(1)
C(2)–C(1)–N(1)	119(2)	C(8)–N(2)–C(7)	111(1)
C(3)–C(2)–C(1)	119(2)	C(9)–C(8)–N(2)	111(2)
C(4)–C(3)–C(2)	123(2)	C(10)–C(9)–C(8)	124(2)
C(5)–C(4)–C(3)	116(2)	N(3)–C(9)–C(8)	118(2)
C(4)–C(5)–N(1)	122(2)	N(3)–C(9)–C(10)	118(2)
C(6)–C(5)–N(1)	115(1)	C(11)–C(10)–C(9)	121(2)
C(6)–C(5)–C(4)	123(2)	C(12)–C(11)–C(10)	120(2)
O(1)–C(6)–C(5)	112(2)	C(13)–C(12)–C(11)	119(2)
N(2)–C(6)–C(5)	106(1)	N(3)–C(13)–C(12)	119(2)
N(2)–C(6)–O(1)	116(1)	C(9)–N(3)–Cu	114(1)
C(6)–N(2)–Cu	104(1)	C(13)–N(3)–Cu	124(1)
C(7)–N(2)–Cu	109(1)	C(13)–N(3)–C(9)	122(2)
(c) The H-bonding system (The primed atoms are at x, $\frac{1}{2} - y$, $\frac{1}{2} + z$)			
Br(1)–O(2)	3.32(2)		
Br(1)–O(2′)	3.25(2)		
O(1)–O(2′)	2.71(2)		


(I)

also joins adjacent copper polyhedra through Br····· H–O–H·····Br bonds. This hydrogen-bonded network and the packing in the unit cell are shown in Figure 2.

The copper(II) polyhedron (Tables II and III) is 'intermediate' between the square pyramidal and trigonal bipyramidal extremes, and similar to a [CuN_3Cl_2] structure described by Huq and Skapski [4]. Other [CuN_3X_2] type structures [5–15] are generally quite near either extreme, with the 'square

TABLE III. Equations of the Least-squares Planes. These are given in the form $lX + mY + nZ = d$ (where X, Y and Z are Co-ordinates in Å referred to the axes *a*, *b* and *c**). Deviations (Å) of various atoms from these planes are given in square brackets. Angles between some of the planes are listed at the end of the Table.

	l	*m*	*n*	*d*
Plane (1):				
N(1), N(2), N(3)	−0.4456	0.8836	−0.1442	1.8722
[Cu −0.06, Br(1) 2.24, Br(2) −1.91, C(5) 0.43, C(6) 0.88, C(8) 0.59, C(9) 0.30]				
Plane (2):				
N(1), C(1)–C(5)	−0.4091	0.7910	−0.4550	0.7700
[Cu 0.06, C(6) 0.17]				
Plane (3):				
N(3), C(9)–C(13)	−0.4318	0.8415	−0.3247	1.3134
[Cu −0.04, C(8) 0.14]				
Plane (4):				
N(2), Br(1), Br(2)	0.8976	0.4407	−0.0102	2.3117
[Cu −0.004]				
Plane (5):				
Cu, Br(1), Br(2)	0.8976	0.4408	−0.0073	2.3150
[N(2) 0.01]				

Angles between planes (°)

(1)–(2)	18.8	(1)–(4)	89.5
(1)–(3)	10.7	(2)–(3)	8.1

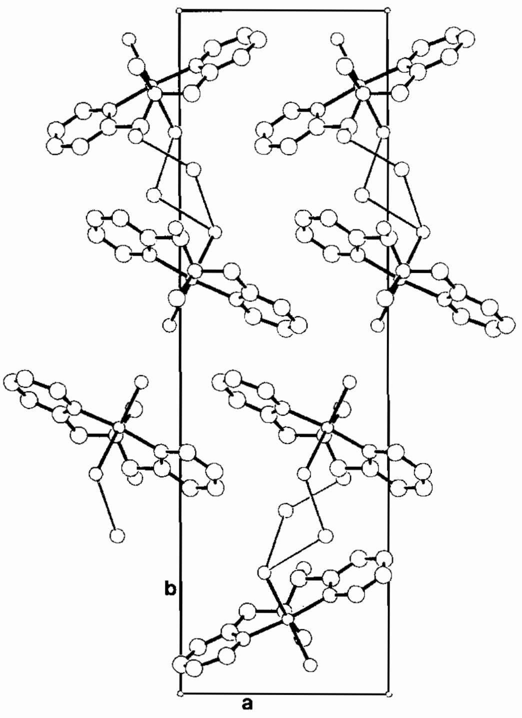


Figure 2. (*a*) A projection perpendicular to the *110* plane, showing the packing of the molecules in the unit cell.

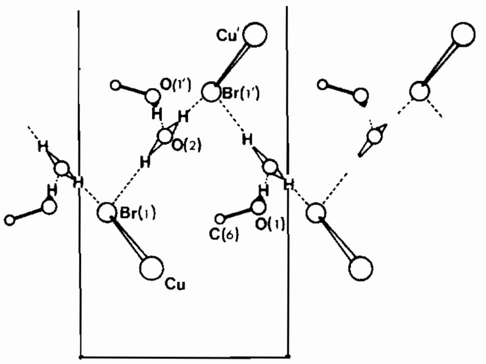


Figure 2. (*b*) A projection down *a* showing the infinite H-bonded network. Hydrogen atoms are included in their most probable positions.

pyramidal' structures [5, 9, 11] sometimes having another more weakly bound (longer bond) ligand in the 'sixth co-ordination site'. In the present case, as with the structure of ref. 4, the unequal Cu–X bond lengths [Cu–Br = 2.598(3) and 2.436(3) Å] immediately suggest the square pyramidal extreme, but the bond angles (Tables II and III) are closer to those of a trigonal bipyramid. Bond lengths to the copper are in the usual range. The longer Cu–Br bond is to the bromine which is involved in hydrogen-bonding.

In the trigonal bipyramidal formalism, the pyridyl nitrogens occupy axial sites and the tertiary nitrogen and the bromines are equatorial ligands. At first sight therefore, with Cu–N(pyridyl) = 1.98(1) Å and Cu–N (tert.) = 2.07(1) Å, the structure fits into the pattern of long equatorial and short axial bond lengths usually found in trigonal bipyramidal copper(II) structures [4, 8, 16–18]. However, the meaning of such an observation in the present case is doubtful since covalent bonds to tertiary amines are usually longer than those to pyridyl nitrogens. Similarly, the comments of Ziolo *et al.* [8] on the different Cu–N bond lengths in [Cu(Et$_4$dien)(N$_3$)Br] must be taken *cum grano salis* for the same sorts of reasons. We do not deny that equatorial bond lengths tend to be longer than axial ones in copper(II) trigonal bipyramids, but note that this is best defined in the known structures [4, 7, 18] with unidentate ligands. The known structures involving multidentate ligands [8, 15–17], including the present one, merely fit the classification without proving it.

Bond lengths and angles within the ligand I (Table II) are, within the limits of accuracy, unexceptionable.

It is an unusual ligand: carbinolamines are rare in known carbon chemistry. However, its formation in the reaction mixture can be readily rationalised. 2-Picolylmethylamine is clearly susceptible to oxidative de-amination. This was documented [19] for 2-picolylamine in 1936. The resulting pyridine-2-aldehyde can then condense with a further molecule of the parent amine to give, in labile equilibrium, the ligand I. Only a very low concentration of I need be present in the solution to account for the copper(II) compound crystallising out. Although we have no information on the robustness of the free ligand, it is likely that it is stabilised by bonding to the metal.

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