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Copper Quinaldinate Monohydrate [Aquabis(2-quinolinecarboxylato)copper(II)]; Pentacoordinate Copper

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Abstract. $[Cu(C_{10}H_6NO_2)_2(H_2O)]$, $M_r = 425\cdot9$, monoclinic, $P2_1/c$, $a = 7\cdot756$ (1), $b = 7\cdot628$ (2), $c = 29\cdot573$ (5) Å, $\beta = 95\cdot31$ (1)°, $V = 1742\cdot2$ (6) Å^3, $Z = 4$, $D_x = 1\cdot62$, $D_m = 1\cdot60$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0\cdot71073$ Å, $\mu = 13\cdot4$ cm^{-1}, $F(000) = 868$, $T = 293$ (1) K, $R = 0\cdot050$ for 2816 reflections. The Cu atom is pentacoordinate, with its configuration intermediate between that of a trigonal bipyramid and a rectangular pyramid. The ligand–metal–ligand angles are distorted in the direction corresponding to a Berry-type displacement. Comparison of the dihedral angles of the pyramidal faces with the limiting values of the two forms indicates a Berry displacement of 49%. The quinaldinic acid acts as a bidentate ligand, bonded through an apical N and an equatorial carboxylate O (referred to the trigonal bipyramid). The water molecule occupies the third equatorial position. The copper–ligand distances are 1·954 (3) and 1·962 (3) Å for Cu—O and 2·012 (3) and 2·014 (3) Å for Cu—N; the copper–water distance is 2·143 (3) Å.

Introduction. The structure analysis of the title compound is a continuation of the investigation of metal complexes of aromatic and heterocyclic amino acids (Haendler, 1985; Boudreau, Boudreau & Haendler, 1983; Boudreau & Haendler, 1981; Lange & Haendler, 1975). Quinaldinic acid is a metabolite of tryptophan and has also been suggested as a gravimetric reagent for several metals (Ray & Bose, 1933; Prodinger, 1940). The Cu complex is an unexpected monohydrate. It contains pentacoordinated Cu and is intermediate between the trigonal-bipyramidal and rectangular-pyramidal structures, analogous to examples discussed in detail by Holmes (1984).

Experimental. Crystals were grown by reactive diffusion between a methanol solution of copper(II) acetate monohydrate and an ethanol solution of quinaldinic acid, in a 1:4 ratio (Martin & Haendler,

1978). Density of a bulk sample was determined pycnometrically in toluene.

The crystal used was an aquamarine rectangular parallelepiped, $0\cdot20 \times 0\cdot30 \times 0\cdot50$ mm. Nicolet four-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. 15 reflections ($2\theta > 20°$) for measurement of lattice parameters at 293 (1) K. No absorption correction ($\mu = 13\cdot4$ cm^{-1}). Max. $\sin\theta/\lambda = 0\cdot650$ Å^{-1}. h 0 to 10, k 0 to 9, l −38 to 38. 6 check reflections, frequency 300, no indication of deterioration or alignment changes. No extinction correction. 3989 reflections measured, 888 unobserved with $I < 3\sigma(I)$. Because of difficulties in interpretation of the Patterson map, Cu atoms located by symbolic addition (Ahmed, 1973); remaining non-hydrogen atoms located by *DIRDIF* (Beurskens & Noordik, 1971; Gould, van den Hark & Beurskens, 1975; van den Hark, Prick & Beurskens, 1976). Least-squares refinement on F, block-diagonal approximation, isotropic and anisotropic thermal parameters. Positions of the ring H atoms calculated; water H atoms from difference Fourier map after further refinement. Final block-diagonal refinement, with 2816 reflections (285 low-intensity reflections with $\Delta F/F_o > 0\cdot3$ omitted), anomalous dispersion for Cu, and $B = 5\cdot0$ Å^2 for H atoms, converged at $R = 0\cdot050$, $wR = 0\cdot030$, $w = 1/\sigma^2(F_o)$. $(\Delta/\sigma)_{max} = 0\cdot43$, exclusive of H shifts. $S = 1\cdot53$. Final difference map showed max. and min. peaks of 0·89 and −1·34 e Å^{-3}. Error analysis showed no systematic errors as functions of $\sin^2\theta$ or F_o. No significant correlations. Atomic scattering factors for the nonhydrogen atoms from Hanson, Herman, Lee & Skillman (1964), and for H from Stewart, Davidson & Simpson (1965). Correction terms for anomalous dispersion for Cu from *International Tables for X-ray Crystallography* (1974). National Research Council of Canada programs (Ahmed, 1973) were used for all calculations; *ORTEP*II (Johnson, 1976) for the thermal-ellipsoid plot.

Table 1. *Final positional parameters and equivalent Debye–Waller factors*

$$B_{eq} = \tfrac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
Cu	0·3396 (0·7)	0·7289 (0·7)	0·1192 (0·2)	2·99
O(1)	0·2377 (4)	0·5030 (4)	0·1005 (1)	4·00
O(2)	0·5582 (4)	0·8284 (4)	0·1465 (1)	4·21
O(3)	0·8303 (4)	0·8672 (5)	0·1311 (1)	5·61
O(4)	0·1634 (5)	0·2494 (4)	0·1302 (1)	5·78
O(5)	0·1433 (4)	0·9212 (4)	0·1017 (1)	3·54
N(1)	0·2618 (4)	0·6567 (4)	0·1796 (1)	2·79
N(2)	0·4536 (4)	0·7620 (5)	0·0614 (1)	3·13
C(1)	0·2019 (6)	0·4046 (6)	0·1320 (1)	3·45
C(2)	0·2094 (6)	0·4932 (6)	0·1784 (1)	2·97
C(3)	0·1649 (6)	0·4016 (6)	0·2168 (1)	3·80
C(4)	0·1816 (6)	0·4862 (6)	0·2580 (1)	3·96
C(5)	0·2376 (5)	0·6598 (6)	0·2606 (1)	3·27
C(6)	0·2604 (6)	0·7521 (7)	0·3023 (1)	4·35
C(7)	0·3112 (6)	0·9220 (6)	0·3033 (1)	4·52
C(8)	0·3429 (5)	1·0093 (6)	0·2628 (1)	3·86
C(9)	0·3244 (5)	0·9249 (6)	0·2221 (1)	3·24
C(10)	0·2739 (4)	0·7483 (6)	0·2201 (1)	2·86
C(11)	0·6767 (5)	0·8375 (6)	0·1189 (1)	3·63
C(12)	0·6175 (5)	0·8080 (6)	0·0695 (1)	3·14
C(13)	0·7279 (6)	0·8293 (6)	0·0349 (1)	4·08
C(14)	0·6625 (5)	0·7991 (7)	−0·0086 (1)	4·36
C(15)	0·4889 (5)	0·7512 (6)	−0·0189 (1)	3·74
C(16)	0·4141 (6)	0·7228 (7)	−0·0635 (1)	5·01
C(17)	0·2446 (6)	0·6807 (7)	−0·0713 (1)	5·23
C(18)	0·1382 (6)	0·6644 (6)	−0·0353 (1)	4·45
C(19)	0·2078 (5)	0·6901 (6)	0·0083 (1)	3·86
C(20)	0·3848 (5)	0·7352 (6)	0·0177 (1)	3·16
H(51)	0·156 (6)	1·056 (7)	0·109 (2)	
H(52)	0·039 (7)	0·874 (7)	0·109 (2)	

Table 2. *Selected bond distances* (Å) *and angles* (°)

Cu–O(1)	1·954 (3)	O(1)–C(1)	1·248 (5)	
Cu–N(1)	2·014 (3)	C(1)–O(4)	1·221 (5)	
Cu–O(2)	1·962 (3)	C(1)–C(2)	1·526 (6)	
Cu–N(2)	2·012 (3)	C(2)–N(1)	1·311 (5)	
Cu–O(5)	2·143 (3)	O(2)–C(11)	1·286 (5)	
O(1)–N(1)	2·608 (4)	C(11)–O(3)	1·233 (5)	
O(2)–N(2)	2·623 (4)	C(11)–C(12)	1·507 (5)	
O(1)–N(2)	2·898 (4)	C(12)–N(2)	1·319 (5)	
O(2)–N(1)	2·894 (4)	O(5)–H(51)	1·05 (5)	
O(5)···O(4)*	2·642 (4)	O(5)–H(52)	0·93 (5)	
O(5)···O(3)	2·685 (4)	H(51)···O(4)	1·60 (5)	
		H(52)···O(3)	1·80 (5)	

O(1)–Cu–O(2)	140·3 (1)	Cu–N(1)–C(2)	110·7 (3)
O(1)–Cu–O(5)	106·0 (1)	Cu–N(2)–C(12)	111·8 (2)
O(2)–Cu–O(5)	113·7 (1)	N(1)–C(2)–C(1)	115·6 (3)
O(1)–Cu–N(1)	82·1 (1)	N(2)–C(12)–C(11)	114·7 (3)
O(1)–Cu–N(2)	93·9 (1)	O(1)–C(1)–C(2)	114·4 (4)
O(2)–Cu–N(1)	93·4 (1)	O(2)–C(11)–C(12)	115·8 (3)
O(2)–Cu–N(2)	82·5 (1)	Cu–O(1)–C(1)	115·5 (3)
O(5)–Cu–N(1)	97·9 (1)	Cu–O(2)–C(11)	113·6 (2)
O(5)–Cu–N(2)	93·9 (1)	O(1)–C(1)–O(4)	128·4 (4)
N(1)–Cu–N(2)	168·2 (1)	O(2)–C(11)–O(3)	123·5 (4)
H(51)–O(5)–H(52)	114 (4)	O(5)–H(51)···O(4)	167 (4)
		O(5)–H(52)···O(3)	158 (4)

* The dotted line represents a bond between atoms in different molecules.

Discussion. The final positional parameters are given in Table 1,* and principal bond distances and angles in Table 2. One half the unit cell is shown in projection in Fig. 1; the thermal-ellipsoid plot is in Fig. 2, the ring H atoms being omitted. The Cu atom is penta-coordinated. The quinaldinate ligand is bidentate, forming a five-membered chelate ring with the Cu. The water molecule occupies the fifth coordination site. The ligand distances vary slightly, 1·954–1·962 Å for Cu–O, 2·012–2·014 Å for Cu–N. The Cu–O distance for the water is 2·143 Å. There is indication of hydrogen bonding between the H atoms of the water and O(3) and O(4) of adjacent molecules.

In pentacoordination there exists the possibility of structures intermediate between the two extremes, the trigonal bipyramid (t.b.p.) and the square (s.p.) or rectangular (r.p.) pyramid. Holmes (1984), in an excellent review, has discussed the transition charac-teristics and parameters for these systems, based on the Berry intramolecular ligand-exchange process (Holmes & Deiters, 1977; Muetterties & Guggenberger, 1974; Berry, 1960). Constraints imposed by polydentate ligands can influence the configuration; a bidentate ligand permits more freedom of motion. Unequal bond character (N vs O) favors axial-equatorial sites of t.b.p. rather than cis-basal positions of s.p. or r.p. A comparison of the nine dihedral angles with idealized values places the complex directly on the Berry coordinate line, at 49% displacement from t.b.p. Table 3 lists the characterization parameters for the four atomic motions.
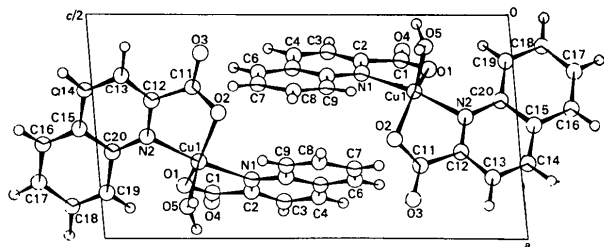
Fig. 1. Projection of one-half the unit cell of copper(II) quinaldinate monohydrate, as viewed along the [010] direction.
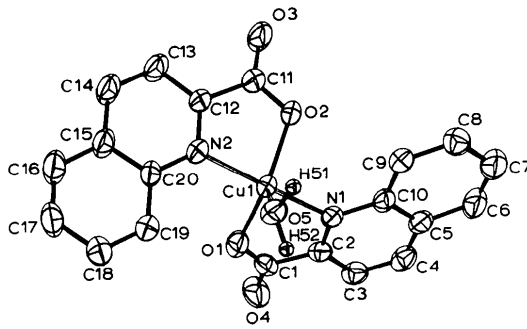

Fig. 2. Thermal-ellipsoid plot of copper(II) quinaldinate monohydrate.

Table 3. *Characteristic Berry ligand displacement motions*

	Value (°) observed	Value (°) expected
N(1)–Cu–N(2)	168·2	<180
O(2)–Cu–O(1)	140·2	>120
O(2)–Cu–O(5)	113·7	<120
O(5)–Cu–O(1)	106·0	<120
δ_{24}*	26·0	$0 < \delta < 53\cdot0$

* δ_{24} is the dihedral angle between the two faces of the t.b.p. that convert to the basal plane of the r.p.

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Di-μ-chloro-bis[bis(2-methylpyridine)copper(I)]

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Abstract. [CuCl(C₆H₇N)₂]₂, $M_r = 570\cdot50$, triclinic, $P\bar{1}$, $a = 8\cdot908$ (3), $b = 9\cdot038$ (4), $c = 9\cdot532$ (3) Å, $\alpha = 95\cdot06$ (3), $\beta = 117\cdot42$ (3), $\gamma = 109\cdot06$ (3)°, $V = 617\cdot2$ Å³, $Z = 1$, $D_x = 1\cdot535$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 19\cdot65$ cm⁻¹, $F(000) = 292$, $T = 193$ K, $R = 0\cdot038$ for 1171 observed reflections. The Cu atoms are pseudo-tetrahedrally coordinated by two bridging Cl atoms and two N atoms from the nitrogen bases. The geometry of the $N_4Cu_2Cl_2$ core is very similar to that of the $N_4Cu_2Br_2$ core of the isotypic complex [CuBr(2-methylpyridine)₂]₂.

Introduction. Copper(I) complexes are of current interest because of the metal–metal interaction in systems with d^{10} electronic configuration. Dimeric adducts of general formula $(L_2CuX)_2$ with $L =$ nitrogen base have been structurally characterized for a considerable number of copper–iodine complexes (Healy, Pakawatchai & White, 1983; Hiller, 1984). Only one

similar structure is known for $X = $ Br, [CuBr(2-methylpyridine)₂]₂ (Schramm, Pierre & Hiller, 1984). The title compound is the first example of the formula $(L_2CuX)_2$ with $X = $ Cl. Further examples with $L = $ 2,4-dimethylpyridine are in preparation (Healy, 1985).

Experimental. Compound prepared by the reaction of CuCl in acetonitrile with 2-methylpyridine in acetone; crystallization on cooling to 250 K. Compared with the adducts of CuI and CuBr, the complex is more sensitive in the presence of oxygen. Needles with yellow-luminescence properties, $0\cdot10 \times 0\cdot10 \times 0\cdot5$ mm, Enraf–Nonius CAD-4 diffractometer (graphite monochromator), all investigations at 193 K to avoid decomposition. Unit-cell parameters from 2θ values of 25 reflections ($10 < 2\theta < 21°$); triclinic, $P\bar{1}$ confirmed by structure solution. 3128 reflections ($\theta \le 22°$) measured, $h \pm 9$, $k \pm 10$, $l \pm 9$. No significant intensity variation for three standard reflections. Empirical