

Structure of Bis[2-methyl-1,1-di(2-pyridyl)-2-propanol]copper(II) Dichloride Dihydrate

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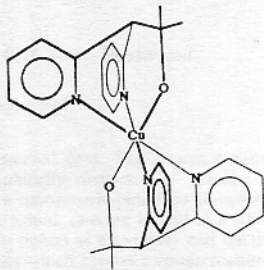
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Abstract. $C_{28}H_{32}CuN_4O_3 \cdot 2Cl \cdot 2H_2O$, $M_r = 627.06$, monoclinic, $P2_1/c$, $a = 9.137$ (2), $b = 9.047$ (2), $c = 18.377$ (7) Å, $\beta = 99.10$ (3)°. $V = 1500.4$ (9) Å³, $Z = 4$, $D_x = 1.529$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 0.164$ mm⁻¹, $F(000) = 1308$, $T = 291$ K, $R = 0.028$ for 1768 unique observed reflections. The Cu atom displays an octahedral elongated (4+2) coordination. The four N atoms of two 2-methyl-1,1-di(2-pyridyl)-2-propanol molecules lie in a plane. The two out of plane bonds join the O atoms of the modified methane groups. The complex is monomeric with the Cl as counterions [Cu—Cl(1) = 6.105 (2) Å] and crystallizes with two H₂O molecules. The Cu atom is at an inversion center, so the two organic ligands are completely identical. Cu—N(1) = 2.016 (2), Cu—N(2) = 2.026 (2), Cu—O(2) = 2.294 Å.

Introduction. The methane group that bridges the two pyridines rings of the di(2-pyridyl)methane ligand can undergo different reactions. These reactions take place when the ligand is coordinated with copper(II). The oxidation reaction of the —CH₂—

group to form an alcohol, which coordinates with the copper(II) through the O atom has been described (Garland, Le Marouille, Spodine & Manzur, 1986). The —CH₂— group can also be oxidized to a ketone group by molecular oxygen (Urbach, Knopp & Zuberbühler, 1978). The title compound results from the reaction of the —CH₂— group of the coordinated ligand with acetone:



Experimental. The complex was prepared by addition of 1 mmol of anhydrous CuCl₂ to a solution of 2 mmol of di(2-pyridyl)methane in acetone. The reaction mixture was refluxed for 30 min, in the presence of triethyl orthoformate. The complex precipitated when the solution was cooled. The compound was recrystallized from a mixture of acetonitrile-water. Crystal dimensions 0.16 × 0.18 × 0.05 mm; Enraf-Nonius CAD-4 four-circle diffractometer, cell dimensions from 2θ values of 25 reflections, 5.2 ≤ θ ≤ 10.74°, 3250 integrated reflections collected up to (sinθ)/λ < 0.595 Å⁻¹, ω-2θ scan technique, scan width (1.0 + 0.35tanθ)°, 0 ≤ h ≤ 10, 0 ≤ k ≤ 9, -20 ≤ l ≤ 19; variable scan rate with max. scan time 60 s per reflection, no significant decline in intensities of three standard reflections; no absorption and no time-decay corrections applied (R_{int} = 0.012); 1768 unique reflections with F² > 3σ(F²); structure solution by MULTAN (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982), refined by full-matrix least squares based on F_o weights based on counting statistics; 1/w = σ(F²)⁻² = 1/[(σ(I)² + (0.04)I²)] (Stout & Jensen, 1968). Refined parameters: x, y, z, β_{ij} for Cu, Cl, O, N and C atoms; x, y, z for H atoms. 233 variables and 1768 observations with final R = 0.028, wR = 0.029 and S = 0.88 (residual Δρ ≤ 0.24 e Å⁻³, largest shift-to-e.s.d. in the last cycle 0.29). Atomic scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974, Vol. IV); all computer programs from Enraf-Nonius SDP-Plus (Frenz, 1983).

Discussion. Table 1* lists the fractional atomic coordinates of non-H atoms, Table 2 the bond lengths and angles.

The structure consists of discrete centrosymmetrical [Cu(C₁₄H₁₆N₂O)₂]⁺ cations (Fig. 1) and chloride ions. There is a hydrogen bond between the O atoms of the 2-methyl-1,1-di(2-pyridyl)-2-propanol ligands and the H atoms of the water molecules that exist in the lattice [O(2)—H...O(1) = 2.63 (5) Å, and the angle O(2)—H...O(1) = 177 (3)°].

The coordination sphere can be described as an elongated octahedron where the basal plane is formed by the four N atoms of the 2-methyl-1,1-di(2-pyridyl)-2-propanol ligands. The octahedron is completed by two large apical distances provided by the Cu—O bonds corresponding to the alcohol group Cu—O(2) = 2.294 (2) Å as compared with the shorter basal copper-ligand bonds: Cu—N(1) = 2.016 (2) and Cu—N(2) = 2.026 (2) Å. The basal

Table 1. Atomic positional parameters and B_{eq} (Å²) values for compound (1)

$$B_{eq} = (4/3)[\sigma^2 B(1,1) + \sigma^2 B(2,2) + \sigma^2 B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	B _{eq}
Cu	0.000	0.000	0.000	2.333 (8)
Cl(1)	-0.40030 (9)	0.40661 (9)	0.20481 (4)	4.03 (2)
O(1)	0.3545 (3)	0.1543 (3)	0.1716 (2)	6.09 (7)
O(2)	0.0850 (2)	0.0695 (2)	0.0956 (1)	3.60 (4)
N(1)	-0.1467 (2)	-0.0695 (3)	0.0638 (1)	2.64 (5)
N(2)	-0.1454 (2)	0.1644 (3)	-0.0339 (1)	2.55 (5)
C(1)	-0.1843 (3)	-0.2119 (3)	0.0676 (2)	3.31 (6)
C(2)	-0.2844 (3)	-0.2806 (4)	0.1517 (2)	4.42 (7)
C(3)	-0.3483 (3)	-0.1586 (4)	0.1474 (2)	3.83 (7)
C(4)	-0.3125 (3)	-0.0136 (4)	0.1026 (1)	2.77 (6)
C(5)	-0.2101 (3)	0.0306 (3)	0.0959 (2)	2.94 (6)
C(6)	-0.1722 (3)	0.2305 (4)	0.1340 (2)	3.35 (6)
C(7)	-0.0170 (3)	0.1801 (5)	0.2146 (2)	5.23 (9)
C(8)	0.0040 (4)	0.3961 (4)	0.1299 (2)	5.11 (9)
C(9)	0.0101 (4)	0.2406 (3)	0.1069 (1)	2.68 (6)
C(10)	-0.3012 (3)	0.3565 (4)	-0.0034 (2)	3.84 (7)
C(11)	-0.3372 (4)	0.3953 (4)	-0.0762 (2)	4.28 (8)
C(13)	-0.2797 (3)	0.3139 (4)	-0.1279 (2)	3.83 (7)
C(14)	-0.1847 (3)	0.2004 (3)	-0.1052 (2)	3.19 (6)

Table 2. Selected bond distances (Å) and bond angles (°) with e.s.d.'s in parentheses

Cu—N(1)	2.016 (2)	N(2)—H(14)	1.93 (4)
Cu—N(2)	2.026 (2)	C(1)—C(2)	1.383 (5)
Cu—O(2)	2.294 (2)	C(2)—C(3)	1.370 (5)
O(1)—H(1)	0.90 (5)	C(3)—C(4)	1.357 (5)
O(1)—H(2)	0.94 (5)	C(4)—C(5)	1.399 (4)
O(1)—H(3)	1.59 (4)	C(5)—C(6)	1.496 (4)
O(2)—C(7)	1.422 (4)	C(6)—C(7)	1.522 (5)
O(2)—H(2)	1.04 (4)	C(6)—C(10)	1.505 (4)
N(1)—C(1)	1.337 (4)	C(7)—C(8)	1.532 (5)
N(1)—C(5)	1.340 (4)	C(7)—C(9)	1.522 (5)
N(1)—H(1)	1.97 (4)	C(10)—C(11)	1.376 (4)
N(2)—C(10)	1.348 (4)	C(11)—C(12)	1.373 (5)
N(2)—C(14)	1.342 (4)	C(12)—C(13)	1.370 (5)
		C(13)—C(14)	1.367 (5)
N(1)—Cu—N(2)	86.79 (9)	C(4)—C(5)—C(6)	120.7 (3)
H(1)—O(1)—H(2)	113.0 (4)	C(5)—C(6)—C(7)	113.8 (3)
H(1)—O(1)—H(3)	125.0 (3)	C(5)—C(6)—C(10)	110.9 (3)
H(2)—O(1)—H(3)	114.0 (3)	C(7)—C(6)—C(10)	113.9 (3)
C(7)—O(2)—H(2)	112.0 (2)	O(2)—C(7)—C(8)	107.2 (3)
Cu—N(1)—C(1)	122.0 (2)	O(2)—C(7)—C(10)	110.3 (3)
Cu—N(1)—C(5)	118.8 (2)	O(2)—C(7)—C(9)	108.3 (3)
C(1)—N(1)—C(5)	119.2 (3)	C(6)—C(7)—C(8)	109.8 (3)
Cu—N(2)—C(10)	118.9 (2)	C(6)—C(7)—C(9)	111.1 (3)
Cu—N(2)—C(14)	122.6 (2)	C(8)—C(7)—C(9)	110.1 (3)
C(10)—N(2)—C(14)	118.4 (3)	N(2)—C(10)—C(6)	118.0 (3)
N(1)—C(1)—C(2)	118.5 (4)	N(2)—C(10)—C(11)	120.9 (3)
C(1)—C(2)—C(3)	122.4 (3)	C(6)—C(10)—C(11)	121.1 (3)
C(2)—C(3)—C(4)	119.5 (3)	C(10)—C(11)—C(12)	120.2 (3)
C(3)—C(4)—C(5)	120.1 (3)	C(11)—C(12)—C(13)	118.6 (4)
N(1)—C(5)—C(4)	120.3 (3)	C(12)—C(13)—C(14)	119.2 (3)
N(1)—C(5)—C(6)	119.0 (3)	N(2)—C(14)—C(13)	122.6 (3)

plane formed by four N atoms and the Cu atom is planar due to the symmetry of the system. The angle formed by O(2)—Cu—N(1) is 85.6 (6)°, and the one formed with respect to N(2) is 84.8°. The tridentate ligand 2-methyl-1,1-di(2-pyridyl)-2-propanol forms a six-membered ring with the Cu atom which is non-planar. The two planar pyridyl rings form a dihedral angle of 61.8 (6)°, as compared with the value of

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53753 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

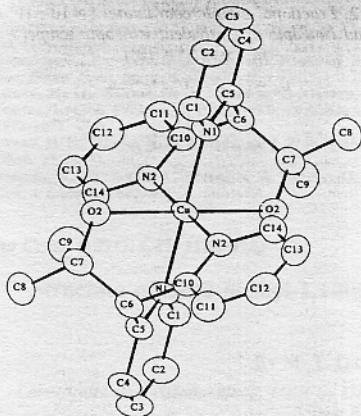


Fig. 1. A perspective view of the molecule with atom numbering. H atoms excluded for clarity.

65.8° for the di(2-pyridyl)methanol ligand in $[\text{Cu}(\text{C}_{11}\text{H}_{10}\text{N}_2)(\text{C}_{11}\text{H}_{10}\text{NO})\text{Cl}]\text{ClO}_4$ (Garland, Le-Marouille, Spodine & Manzur, 1986).

The Cu—O(2) bonds are 2.294 (2) Å, longer than the Cu—O distances usually reported for the alcohol groups [International Tables for X-ray Crystallography (1974, Vols. II and IV)], but shorter than the one found for the copper(II) complex with the di(2-pyridyl)methanol ligand, whose Cu—OH distance is 2.660 (5) Å. The angles of the 2-propanol group are

those corresponding to tetrahedral symmetry. The C—O bond is 1.422 Å which is comparable with the usual distance for this group.

The C—N bonds are more similar to those found for the dimeric dibromo[di(2-pyridyl)methane]-copper(II) complex (Garland, Grandjean, Spodine & Manzur, 1987), than to the ones found for the oxygenated ligand. The other distances and angles of the ligand are approximately as expected.

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