

Structure of (Chloro)(di-2-pyridylmethane)(di-2-pyridylmethanol)copper(II) Perchlorate

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Abstract. $[\text{CuCl}(\text{C}_{11}\text{H}_{10}\text{N}_2)(\text{C}_{11}\text{H}_{10}\text{N}_2\text{O})]\text{ClO}_4$, $M_r = 554.87$, monoclinic, $P2_1/c$, $a = 13.397(4)$, $b = 14.663(2)$, $c = 13.191(3)$ Å, $\beta = 116.81(1)^\circ$, $V = 2313(2)$ Å³, $Z = 4$, $D_x = 1.593$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 1.215$ mm⁻¹, $F(000) = 1132$, $T = 291$ K. Final $R = 0.074$ for 2231 unique observed reflections. This high R value can be explained by the disordered perchlorate anion around which many low spurious peaks still remain after least-squares convergence. The coordination sphere of Cu can be described as an elongated octahedron owing to the Jahn-Teller effect. The basal plane is formed by four N atoms provided by the pyridine rings of the di-2-pyridylmethane and of the di-2-pyridylmethanol moieties respectively. The octahedron is completed by two large apical distances provided by the Cu-Cl(1) bond and by the Cu-O(1) bond, corresponding to the oxygen atom of the dipyridylmethanol.

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Introduction. Synthetic copper complexes serve as suitable models for the natural copper centres in metalloproteins when they mimic some physical or chemical property of the protein site. In the case of the monooxygenases one atom of oxygen is reduced to water while the other is transferred to the substrate (Sigel, 1981). The title compound is an example of monooxygenase activity, since it is obtained as a product of the reaction of di-2-pyridylmethane with molecular oxygen. The hydroxylation reaction is catalysed by the presence of copper(II) and chloride ions.

Experimental. A 1 mmol sample of copper(II) perchlorate complex $[\text{Cu}(\text{AN})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ was dissolved with 1 mmol of copper(II) chloride in freshly distilled methanol and slightly refluxed. After this, 3 mmol of di-2-pyridylmethane dissolved in the same solvent were added to the warm reaction mixture and heated. The reaction mixture was air-saturated, since no precautions were taken to degas the solutions. When cooled, bright blue crystals were formed. The infrared

spectrum did not show the typical stretching frequency of the carbonyl group at 1600–1700 cm^{-1} , thus indicating that oxidation to a ketone had not taken place (Urbach, Knopp & Zuberbühler, 1978).

Crystal dimensions 0.15 × 0.17 × 0.08 mm; Nonius CAD-4 four-circle diffractometer, cell dimensions from 2θ values of 25 reflections, $6.17 \leq \theta \leq 11.65^\circ$, 3602 integrated reflections collected up to $\sin\theta/\lambda \leq 0.595 \text{ \AA}^{-1}$, ω - 2θ scan technique, scan width (1.0 + 0.35 $\tan\theta$), $0 \leq h \leq 15$, $0 \leq k \leq 17$, $-11 \leq l \leq 11$; variable scan rate with max. scan time 60 s per reflection; no significant decline in intensities of three standard reflections; decay 3.2% during 49 h of irradiation; no absorption correction and no time-decay corrections applied, 3406 unique reflections after averaging ($R_{\text{int}} = 0.020$); 2231 reflections with $F^2 > 3\sigma(F^2)$; structure solution by MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) refined by full-matrix least squares based on F_o , weights based on counting statistics: $1/w = \sigma^2(F)$ = $\frac{1}{4}[\sigma^2(I) + (0.05 I^2)/I]$ (Stout & Jensen, 1968); atomic scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974); H atoms placed at idealized positions with fixed isotropic thermal parameters and not refined (5 \AA^2); anisotropic thermal parameters for all other atoms

Table 1. Fractional atomic coordinates and equivalent isotropic $B(\text{Å}^2)$ with e.s.d.'s in parentheses

	x	y	z	B
Cu	0.26239 (8)	0.19527 (7)	0.53352 (9)	2.46 (2)
Cl(1)	0.3321 (2)	0.1247 (2)	0.7355 (2)	3.43 (6)
Cl(2)	0.2507 (2)	-0.2975 (2)	0.4965 (3)	6.57 (9)
O(1)	0.2126 (5)	0.3310 (5)	0.3848 (5)	4.1 (2)
O(2)	0.190 (1)	0.725 (1)	0.550 (1)	13.4 (4)*
O(22)	0.2279 (8)	-0.3741 (7)	0.4330 (8)	8.8 (3)
O(23)	0.182 (1)	-0.240 (2)	0.392 (2)	19.3 (7)*
O(24)	0.3432 (8)	-0.2448 (8)	0.524 (1)	10.6 (4)
N(1)	0.1820 (5)	0.2977 (5)	0.5728 (6)	2.7 (2)
N(2)	0.3955 (5)	0.2805 (5)	0.5879 (6)	2.4 (2)
N(3)	0.3340 (5)	0.1161 (5)	0.4553 (6)	2.6 (2)
N(4)	0.1207 (5)	0.1387 (6)	0.4541 (6)	3.1 (2)
Cl(1)	0.1259 (8)	0.2822 (7)	0.6339 (8)	3.8 (3)
C(2)	0.0764 (7)	0.3541 (9)	0.6647 (8)	4.4 (3)
C(3)	0.0908 (9)	0.4425 (8)	0.6366 (9)	5.1 (3)
C(4)	0.1483 (8)	0.4571 (7)	0.5739 (9)	4.1 (3)
C(5)	0.1925 (7)	0.4826 (7)	0.5445 (7)	2.8 (2)
C(6)	0.3793 (6)	0.3673 (6)	0.5542 (7)	2.5 (2)
Cl(7)	0.4659 (7)	0.4297 (7)	0.5897 (8)	3.3 (2)
Cl(8)	0.5719 (7)	-0.0292 (7)	0.6587 (8)	4.0 (3)
C(9)	0.5892 (7)	0.2105 (7)	0.6936 (8)	3.5 (2)
C(10)	0.4995 (7)	0.3553 (7)	0.6599 (7)	2.9 (2)
C(11)	0.2599 (7)	0.3924 (7)	0.4779 (8)	3.3 (2)
Cl(12)	0.3910 (7)	0.1522 (7)	0.4070 (7)	2.8 (2)
Cl(13)	0.4317 (7)	0.1003 (7)	0.3458 (8)	3.4 (2)
Cl(14)	0.4130 (8)	0.0310 (7)	0.3243 (8)	3.9 (2)
C(15)	0.3354 (8)	-0.0292 (6)	0.3864 (8)	3.5 (2)
C(16)	0.3127 (7)	0.0236 (6)	0.4441 (8)	2.7 (2)
Cl(17)	0.1287 (7)	0.0282 (7)	0.4449 (7)	3.1 (2)
Cl(18)	0.0355 (8)	-0.0243 (8)	0.3848 (9)	4.2 (3)
Cl(19)	-0.0653 (8)	0.0159 (9)	0.3356 (9)	5.7 (3)
Cl(20)	-0.0734 (8)	0.1072 (9)	0.3470 (9)	4.8 (3)
Cl(21)	0.0192 (7)	0.1578 (8)	0.4047 (8)	3.6 (3)
Cl(22)	0.2420 (7)	-0.0130 (7)	0.4973 (8)	3.4 (2)

* Isotropically refined temperature factors.

except for the two disordered O atoms of the perchlorate anion; refinement converged to $R = 0.074$ and $wR = 0.095$; goodness of fit $S = 2.647$ for 298 refined parameters; largest shift over e.s.d. in last cycle 0.50; largest residual peak in final Fourier map 0.88 e \AA^{-3} except for two peaks of 1.34 and 1.1 e \AA^{-3} provided by the disorder of the two O atoms from the perchlorate anion. All computer programs from the Enraf-Nonius package (Frenz, 1978). Final atomic coordinates are given in Table 1 and bond lengths and angles in Table 2.*

* Lists of structure factors, anisotropic thermal parameters, least-squares-planes data and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43235 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

Cu—Cl(1)	2.607 (2)	Cl(2)—Cl(3)	1.384 (11)
Cu—O(1)	2.660 (5)	Cl(3)—Cl(4)	1.376 (11)
Cu—N(1)	2.045 (5)	Cl(4)—Cl(5)	1.379 (9)
Cu—N(2)	2.027 (4)	Cl(5)—Cl(11)	1.524 (9)
Cu—N(3)	2.057 (5)	C(6)—C(7)	1.383 (8)
Cu—N(4)	2.041 (5)	C(6)—C(11)	1.502 (8)
Cl(2)—O(22)	1.351 (7)	Cl(7)—Cl(8)	1.365 (9)
Cl(2)—O(23)	1.515 (15)	Cl(8)—Cl(9)	1.381 (10)
Cl(2)—O(24)	1.362 (7)	Cl(9)—Cl(10)	1.364 (8)
O(1)—Cl(1)	1.420 (8)	Cl(12)—Cl(13)	1.388 (9)
N(1)—Cl(1)	1.346 (8)	Cl(13)—Cl(14)	1.329 (9)
N(1)—Cl(5)	1.326 (7)	Cl(14)—Cl(5)	1.397 (9)
N(2)—Cl(6)	1.333 (7)	Cl(15)—Cl(16)	1.360 (9)
N(2)—Cl(10)	1.345 (7)	Cl(16)—Cl(22)	1.508 (8)
N(3)—Cl(12)	1.308 (7)	Cl(17)—Cl(18)	1.374 (8)
N(3)—Cl(16)	1.380 (7)	Cl(17)—Cl(22)	1.483 (9)
N(4)—Cl(17)	1.341 (8)	Cl(18)—Cl(19)	1.343 (11)
N(4)—Cl(21)	1.344 (8)	Cl(19)—Cl(20)	1.357 (11)
Cl(1)—Cl(2)	1.400 (10)	Cl(20)—Cl(21)	1.347 (9)
Cl(1)—Cu—O(1)	155.0 (1)	Cl(2)—Cl(3)—Cl(4)	119.3 (7)
Cl(1)—Cu—N(1)	91.1 (1)	Cl(3)—Cl(4)—Cl(5)	118.3 (7)
Cl(1)—Cu—N(2)	91.7 (1)	N(1)—Cl(5)—Cl(11)	123.4 (6)
Cl(1)—Cu—N(3)	104.8 (1)	N(1)—Cl(5)—Cl(11)	114.6 (6)
Cl(1)—Cu—N(4)	97.4 (2)	Cl(1)—Cl(5)—Cl(11)	92.7 (5)
O(1)—Cu—N(1)	69.7 (2)	Cl(1)—Cl(5)—Cl(11)	145.3 (5)
O(1)—Cu—N(2)	71.8 (2)	Cl(4)—Cl(5)—Cl(11)	122.0 (6)
O(1)—Cu—N(3)	86.2 (2)	N(2)—Cl(6)—Cl(10)	122.2 (6)
O(1)—Cu—N(4)	99.7 (2)	N(2)—Cl(6)—Cl(11)	112.5 (5)
N(1)—Cu—N(2)	86.4 (2)	Cl(7)—Cl(6)—Cl(10)	114.4 (4)
N(1)—Cu—N(3)	163.7 (2)	Cl(7)—Cl(6)—Cl(11)	122.8 (6)
N(1)—Cu—N(4)	93.5 (2)	Cl(10)—Cl(6)—Cl(11)	145.7 (4)
N(2)—Cu—N(3)	89.4 (2)	C(6)—C(7)—C(8)	118.0 (6)
N(2)—Cu—N(4)	170.9 (2)	Cl(7)—Cl(8)—Cl(9)	119.4 (4)
N(3)—Cu—N(4)	89.2 (2)	N(2)—Cl(6)—Cl(10)	122.2 (6)
O(22)—Cl(2)—O(23)	91.3 (7)	N(2)—Cl(6)—Cl(11)	122.5 (6)
O(23)—Cl(2)—O(24)	124.5 (2)	Cl(6)—Cl(10)—Cl(11)	91.4 (4)
O(23)—Cl(2)—O(24)	92.0 (7)	O(1)—Cl(11)—Cl(5)	106.8 (5)
Cu—O(1)—Cl(1)	88.3 (3)	O(1)—Cl(11)—Cl(6)	130.5 (5)
Cu—N(1)—Cl(1)	121.8 (4)	Cl(5)—Cl(11)—Cl(6)	108.6 (5)
Cu—N(1)—Cl(5)	118.9 (4)	N(3)—Cl(12)—Cl(13)	122.0 (6)
Cl(1)—N(1)—Cl(5)	119.1 (5)	Cl(12)—Cl(13)—Cl(14)	120.2 (6)
Cu—N(2)—Cl(6)	119.1 (4)	Cl(13)—Cl(14)—Cl(15)	118.7 (6)
Cu—N(2)—Cl(10)	122.3 (4)	Cl(14)—Cl(15)—Cl(16)	119.9 (6)
C(6)—N(2)—Cl(10)	118.8 (5)	N(3)—Cl(16)—Cl(15)	120.2 (6)
Cu—N(3)—Cl(12)	121.5 (4)	Cl(16)—Cl(15)—Cl(12)	116.3 (5)
Cu—N(3)—Cl(16)	119.2 (4)	Cl(15)—Cl(16)—Cl(22)	122.5 (6)
Cl(12)—N(3)—Cl(16)	119.0 (4)	N(4)—Cl(17)—Cl(18)	121.2 (7)
Cu—N(4)—Cl(17)	119.8 (4)	Cl(18)—Cl(17)—Cl(19)	115.8 (5)
Cu—N(4)—Cl(21)	121.2 (5)	Cl(18)—Cl(17)—Cl(22)	120.9 (6)
Cl(17)—N(4)—Cl(21)	118.9 (6)	Cl(17)—Cl(18)—Cl(19)	119.1 (7)
N(1)—Cl(5)—Cl(11)	120.8 (7)	Cl(18)—Cl(19)—Cl(20)	119.5 (7)
Cl(2)—Cl(1)—Cl(5)	90.6 (5)	Cl(19)—Cl(20)—Cl(21)	120.8 (7)
Cl(1)—Cl(2)—Cl(3)	119.1 (7)	N(4)—Cl(21)—Cl(20)	120.8 (7)
		Cl(16)—Cl(22)—Cl(17)	111.4 (5)

Discussion. The structure consists of discrete [Cu-Cl(C₁₁H₁₀N₂)(C₁₁H₁₀NO)]⁺ cations (Fig. 1) and perchlorate anions. The crystal is stabilized by van der Waals contacts between the O atom of the 2,2'-dipyridylmethanol and the Cl atom.

The coordination sphere can be described as an elongated octahedron where the basal plane is formed by the four N atoms of the di-2-pyridylmethane moiety and of the di-2-pyridylmethanol moiety. The octahedron is completed by two large apical distances provided by the Cu—Cl(1) bond and by the Cu—O(1) bond corresponding to the alcohol group [Cu—Cl(1) = 2.607 (2) and Cu—O(1) = 2.660 (5) Å, compared with the basal copper—ligand bonds: Cu—N(1) = 2.045 (5), Cu—N(2) = 2.027 (4), Cu—N(3) = 2.057 (5) and Cu—N(4) = 2.041 (5) Å].

The unweighted mean plane through the four N atoms of the complex, N(1)—N(2)—N(3)—N(4), shows a lack of planarity with out-of-plane displacements of 0.063, -0.065, 0.064 and -0.062 Å respectively, while the copper atom is displaced by 0.223 Å in the direction of the Cl atom. The dihedral angle between the planes through Cu—N(1)—N(2) and Cu—N(3)—N(4) is 18.1°, indicating a distortion towards tetrahedral geometry.

The bidentate ligand di-2-pyridylmethane forms a six-membered chelate ring with the Cu atom which is non-planar. The dihedral angle formed by the two pyridyl rings is 64.0°. Fackler (1985) found a dihedral angle of 59.1° for the same ligand in a distorted tetrahedral copper(I) complex, bis(di-2-pyridylmethane)copper(I) perchlorate.

The tridentate ligand di-2-pyridylmethanol also forms a six-membered ring with the Cu atom which is non-planar. In this case the two planar pyridyl rings form a dihedral angle of 65.8°.

The carbon atoms, C(2) and C(11), which bridge the two pyridyl rings in both ligands are in opposite directions with respect to the basal plane of the octahedron.

The distance of the C(11)—O(1) bond in the alcohol group is 1.420 (8) Å, which is comparable with the usual distance for these groups (Turpeinen, Hämäläinen & Ahlgren, 1985). The Cu—O(1) bond is 2.660 (5) Å, which is much longer than the usual value reported for Cu—O distances in alcohol groups. For example, Viossat, Khodadad, Rodier & Cadot (1985) report Cu—O bonds whose values are 2.146 (4) and 2.165 (3) Å for neutral ethanol ligands and 2.009 (2) Å for an anionic ethanolato ligand.

The values usually reported for terminal Cu—Cl bonds have a mean value of 2.2 Å (Viossat, Khodadad, Rodier & Cadot, 1985; De Munno & Bruno, 1984). The complex studied presents a terminal Cu—Cl(1) bond of 2.607 (2) Å. A similar high value is found in dichloro(*N*-pyridylmethylene)histamine-*N,N'* copper hemihydrate reported by Nepveu & Walz (1985).

The high thermal parameters indicate that the anion is disordered, as is commonly observed for perchlorate.

Distances and angles of the di-2-pyridylmethane ligand are approximately as expected and require no further comment.

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References

- DE MUNNO, G. & BRUNO, G. (1984). *Acta Cryst.* **C40**, 2022-2024.
- FAKLER, J. P. (1985). Personal communication.
- FRENZ, B. A. (1978). *The Enraf-Nonius CAD-4 SDP - A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Determination. In Computing in Crystallography*, edited by H. SCHENK, R. OLTROP-HÄZEKAMP, H. VAN KONINGSVELD, & G. C. BASSI. Delft Univ. Press.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- NEPVEU, F. & WALZ, L. (1985). *Acta Cryst.* **C41**, 332-334.
- SIHEL, H. (1981). In *Metal Ions in Biological Systems*. Vol. XIII. New York and Basel: Marcel Dekker, Inc.
- STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*. New York: Macmillan.
- TURPEINEN, U., HÄMÄLÄINEN, R. & AHLGRÉN, M. (1985). *Acta Cryst.* **C41**, 1728-1730.
- URBACH, F. L., KNOPP, U. & ZUBERBÜHLER, A. D. (1978). *Helv. Chim. Acta*, **61**(3), 1097-1106.
- VIOSAT, B., KHODADAD, P., RODIER, N. & CADOT, M. (1985). *Acta Cryst.* **C41**, 535-537.

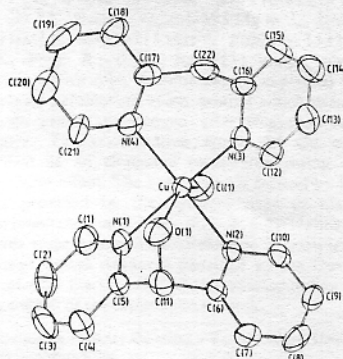


Fig. 1. A perspective view of the molecule with atom numbering; hydrogen excluded for clarity.