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Aqua-μ-chloro-trichloro-μ-[3,6-di(2-pyridyl)pyridazine]-dicopper(II), [Cu₂Cl₄(H₂O)(C₁₄H₁₀N₄)]

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Abstract. $M_r = 521 \cdot 15$, monoclinic, $P2_1/c$, $a = 9 \cdot 809$ (1), $b = 9 \cdot 212$ (1), $c = 19 \cdot 316$ (2) Å, $\beta = 100 \cdot 4$ (1)°, $V = 1716 \cdot 7$ (6) Å³, $Z = 4$, D_m(by flotation) $= 2 \cdot 02$, $D_x = 2 \cdot 016 \text{ g cm}^{-3}$, Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å, $\mu = 30 \cdot 57 \text{ cm}^{-1}$, $F(000) = 1032$, $T = 293$ K, final conventional $R = 0 \cdot 048$ for 1227 unique observed reflections. The complex is the same as that previously reported [De Munno, Denti & Dapporto (1983). *Inorg. Chim. Acta*, **74**, 199–203], but in a different environment. It consists of a binuclear unit containing a bridging tetradentate organic ligand, two Cu atoms, two terminal Cl atoms and a Cl bridge. Both Cu atoms are five-coordinated, the apical sites being occupied by a Cl atom and a water molecule.

Introduction. Several μ-OH binuclear Cu^{II} complexes with the tetradentate ligand 3,6-di(2-pyridyl)pyridazine have been synthesized and their structures determined (Ghedini, De Munno, Denti, Manotti Lanfredi & Tiripicchio, 1982; Dapporto, De Munno, Bruno & Romeo, 1983; Dapporto, De Munno, Sega & Mealli, 1984). The crystal structure of a monohydrated μ-Cl binuclear Cu^{II} complex with the same ligand has also been recently determined (De Munno, Denti & Dapporto, 1983). These binuclear complexes are interesting since their Cu···Cu separations are similar to those reported in oxyhemocyanins: 3·55 and 3·67 Å from EXAFS studies (Co, Hodgson, Eccles & Lontie, 1981; Brown, Powers, Kincaid, Larrabee & Spiro, 1980). In this paper we report the structure of the anhydrous μ-Cl Cu^{II} complex with the ligand 3,6-di(2-pyridyl)pyridazine.

Experimental. The complex is obtained according to the procedure previously reported (Dapporto, De Munno, Sega & Mealli, 1984). Geeen parallelepiped crystal $0 \cdot 04 \times 0 \cdot 10 \times 0 \cdot 10$ mm, Siemens Stoe diffractometer, scan range $2\theta = 3$–$50°$, graphite-monochromatized Mo $K\alpha$ radiation, ω–θ scan technique. 25 reflections for measuring lattice parameters, $7 < \theta < 15°$. No systematic loss of intensity of three standard reflections ($3\bar{3}6$, $1,\overline{10},10$, $2\bar{1}9$). 1472 measured reflections with $\theta < 25°$, 1227 unique with $I \geq 3\sigma(I)$. R_{int} (from merging equivalent reflections) $0 \cdot 036$. $0 \leq h \leq 11$, $0 \leq k \leq 11$, $-23 \leq l \leq 23$. Absorption ignored. Lp correction. Scattering factors for non-hydrogen atoms (*International Tables for X-ray Crystallography*, 1974, p. 99), and for H atoms (Stewart, Davidson & Simpson, 1965). Anomalous-dispersion corrections (*International Tables for X-ray Crystallography*, 1974, p. 149). Structure solved by Patterson and Fourier techniques (Sheldrick, 1976) and refined by a full-matrix least-squares procedure; $\sum w(|F_o| - |F_c|)^2$ minimized; anisotropic thermal parameters for Cu, Cl, N, O, and C(5), C(6), C(9), C(10) atoms; isotropic for the other C atoms; H of the linked water molecule (from ΔF synthesis) and the other H atoms (calculated) assigned isotropic U of $0 \cdot 04$ Å² and not refined; final

$R = 0.048$, $R_w = 0.048$, $w = 1/\sigma^2$; max. $\Delta/\sigma = 0.056$, max. and min. $\Delta\rho$ excursions 0.068 and -0.032 e Å^{-3}, respectively; VAX/VMS computer of the Università della Calabria; *SHELX* program (Sheldrick, 1976) and *XRAY* system of programs (Stewart, Kundell & Baldwin, 1970).

Discussion. Fig. 1 shows a view of the molecule. Final atomic parameters are reported in Table 1;* bond distances and angles are in Table 2. Both Cu^{II} atoms are five-coordinated with a distorted square-pyramidal geometry. They are coordinated in the basal planes by two N atoms of the organic ligand and by two Cl atoms, one of which is bridging the two metal atoms. The apical positions are occupied by an O atom of a water molecule and by a fourth Cl atom. The greatest

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39658 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
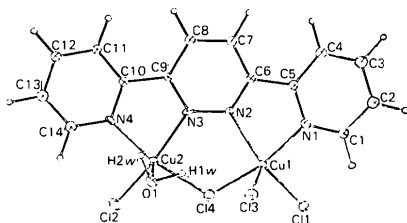

Fig. 1. Molecular structure and labeling scheme.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic (Hamilton, 1959) thermal parameters* (Å$^2 \times 10^3$) *for non-hydrogen atoms*

	x	y	z	U_{eq}
Cu(1)	7634 (2)	−841 (1)	6057 (1)	23 (1)
Cu(2)	6522 (2)	1327 (1)	4530 (1)	25 (1)
Cl(1)	7101 (3)	−595 (3)	7124 (1)	34 (2)
Cl(2)	5403 (4)	3402 (3)	4436 (2)	42 (2)
Cl(3)	9953 (3)	351 (3)	6168 (1)	31 (2)
Cl(4)	6393 (3)	1128 (3)	5664 (1)	40 (2)
O(1)	8843 (7)	1956 (8)	4736 (4)	27 (5)
N(1)	8426 (10)	−2842 (10)	6227 (5)	26 (6)
N(2)	7416 (9)	−1613 (9)	5054 (4)	16 (5)
N(3)	6965 (9)	−792 (9)	4488 (4)	24 (5)
N(4)	6512 (9)	1087 (9)	3513 (4)	17 (5)
C(1)	9053 (12)	−3343 (12)	6834 (5)	26 (3)
C(2)	9523 (13)	−4756 (13)	6910 (6)	36 (3)
C(3)	9294 (13)	−5636 (13)	6332 (6)	37 (3)
C(4)	8661 (13)	−5123 (13)	5700 (6)	32 (3)
C(5)	8264 (12)	−3689 (12)	5653 (5)	23 (6)
C(6)	7682 (12)	−2988 (11)	5003 (5)	16 (6)
C(7)	7480 (11)	−3647 (12)	4344 (5)	25 (3)
C(8)	7065 (12)	−2825 (12)	3768 (5)	27 (3)
C(9)	6875 (10)	−1338 (11)	3855 (5)	15 (6)
C(10)	6563 (12)	−280 (12)	3290 (5)	23 (6)
C(11)	6414 (12)	−633 (12)	2586 (5)	23 (3)
C(12)	6275 (12)	452 (12)	2104 (5)	27 (3)
C(13)	6282 (13)	1863 (13)	2330 (6)	34 (3)
C(14)	6388 (13)	2121 (13)	3035 (6)	30 (3)

Table 2. *Bond distances* (Å) *and angles* (°)

Cu(1)−Cl(1)	2.228 (3)	N(4)−C(14)	1.315 (14)
Cu(2)−Cl(2)	2.195 (4)	C(1)−C(2)	1.380 (16)
Cu(1)−Cl(4)	2.239 (3)	C(2)−C(3)	1.365 (16)
Cu(2)−Cl(4)	2.223 (3)	C(3)−C(4)	1.351 (16)
Cu(1)−Cl(3)	2.500 (3)	C(4)−C(5)	1.376 (16)
Cu(2)−O(1)	2.313 (7)	C(5)−C(6)	1.435 (14)
Cu(1)−N(1)	2.004 (9)	C(6)−C(7)	1.392 (14)
Cu(1)−N(2)	2.038 (8)	C(7)−C(8)	1.347 (14)
Cu(2)−N(3)	2.005 (9)	C(8)−C(9)	1.397 (15)
Cu(2)−N(4)	1.976 (9)	C(9)−C(10)	1.454 (14)
N(1)−C(1)	1.306 (13)	C(10)−C(11)	1.379 (14)
N(1)−C(5)	1.342 (14)	C(11)−C(12)	1.356 (15)
N(2)−N(3)	1.338 (11)	C(12)−C(13)	1.371 (16)
N(2)−C(6)	1.301 (13)	C(13)−C(14)	1.368 (16)
N(3)−C(9)	1.309 (13)	O(1)−H(1w)	0.98 (7)
N(4)−C(10)	1.334 (14)	O(1)−H(2w)	1.04 (8)
Cu(1)−Cl(4)−Cu(2)	106.1 (1)	N(2)−N(3)−C(9)	120.2 (9)
Cl(3)−Cu(1)−Cl(1)	103.8 (1)	Cu(2)−N(4)−C(10)	115.6 (7)
Cl(3)−Cu(1)−N(1)	94.0 (3)	Cu(2)−N(4)−C(14)	126.8 (7)
Cl(3)−Cu(1)−N(2)	99.9 (3)	C(10)−N(4)−C(14)	117.5 (9)
Cl(3)−Cu(1)−Cl(4)	95.9 (1)	N(1)−C(1)−C(2)	121.5 (10)
Cl(1)−Cu(1)−N(1)	95.2 (3)	C(1)−C(2)−C(3)	118.1 (10)
N(1)−Cu(1)−N(2)	78.8 (3)	C(2)−C(3)−C(4)	120.8 (12)
N(2)−Cu(1)−Cl(4)	90.2 (2)	C(3)−C(4)−C(5)	118.3 (10)
Cl(1)−Cu(1)−Cl(4)	91.6 (1)	C(4)−C(5)−N(1)	120.9 (9)
Cl(1)−Cu(1)−N(2)	155.9 (3)	N(1)−C(5)−C(6)	115.5 (9)
Cl(4)−Cu(1)−N(1)	166.3 (3)	C(4)−C(5)−C(6)	123.6 (10)
O(1)−Cu(2)−Cl(2)	104.9 (2)	C(5)−C(6)−C(7)	124.9 (10)
O(1)−Cu(2)−N(4)	91.5 (3)	C(5)−C(6)−N(2)	115.2 (9)
O(1)−Cu(2)−N(3)	92.1 (3)	C(7)−C(6)−N(2)	119.8 (9)
O(1)−Cu(2)−Cl(4)	94.6 (2)	C(6)−C(7)−C(8)	118.9 (10)
Cl(2)−Cu(2)−N(4)	95.9 (3)	C(7)−C(8)−C(9)	118.6 (10)
N(4)−Cu(2)−N(3)	79.2 (3)	C(8)−C(9)−N(3)	120.1 (9)
N(3)−Cu(2)−Cl(4)	90.7 (2)	N(3)−C(9)−C(10)	114.4 (9)
Cl(2)−Cu(2)−Cl(4)	92.1 (1)	C(8)−C(9)−C(10)	125.5 (9)
Cl(2)−Cu(2)−N(3)	162.4 (3)	C(9)−C(10)−C(11)	123.5 (10)
Cl(4)−Cu(2)−N(4)	168.3 (3)	N(4)−C(10)−C(11)	122.5 (10)
Cu(1)−N(1)−C(1)	125.3 (8)	C(9)−C(10)−N(4)	113.9 (9)
Cu(1)−N(1)−C(5)	114.5 (7)	C(10)−C(11)−C(12)	118.9 (10)
C(1)−N(1)−C(5)	120.2 (9)	C(11)−C(12)−C(13)	119.1 (10)
Cu(1)−N(2)−N(3)	122.9 (7)	C(12)−C(13)−C(14)	118.5 (11)
Cu(1)−N(2)−C(6)	115.1 (6)	C(13)−C(14)−N(4)	123.6 (11)
N(3)−N(2)−C(6)	122.0 (8)	H(1w)−O(1)−H(2w)	91.5 (6)
Cu(2)−N(3)−N(2)	124.0 (6)	H(2w)−O(1)−Cu(2)	107.2 (5)
Cu(2)−N(3)−C(9)	115.7 (7)	H(1w)−O(1)−Cu(2)	94.0 (5)

differences with respect to the previously reported complex (De Munno, Denti & Dapporto, 1983), caused probably by the different crystal environment, are in the bond distances of the Cl and O atoms lying at the apices of the two pyramids, which are shorter than in the previous complex [2.500 (3) instead of 2.641 (4) Å and 2.313 (7) instead of 2.386 (9) Å for the Cl and the O atoms respectively]. On the other hand, the Cu—Cl distances in the basal planes are longer than those of the previous complex. In accordance with the shortening of the axial bonds and the lengthening of the basal bonds, the two Cu atoms [Cu(1) and Cu(2)] are displaced, in the new complex, from the mean basal planes by 0.318 (2) and 0.223 (2) Å, respectively, towards the corresponding Cl and O atoms, instead of 0.241 (2) and 0.214 (2) Å, in the previous complex, and the Cl bridging atom is displaced from the Cu(1)—N(2)—N(3)—Cu(2) plane by −0.612 (4) instead of −0.340 (4) Å. The bond-distance variations and the angular distortions around the Cu atoms, which are

found on comparing the two complexes, are small but sufficient to justify the increase of the Cu···Cu separation from 3·51 Å in the previous complex to 3·566 (2) Å in the present one. This separation is the greatest found in Cu^{II} complexes with 3,6-di(2-pyridyl)-pyridazine.

The coordinating water molecule forms an intramolecular hydrogen bond with the apical Cl atom [O(1)–H(1w)···Cl(3) 3·152 (8), H(1w)···Cl(3) 2·28 (7) Å, O(1)–H(1w)···Cl(3) 148 (6)°] and an intermolecular one with the apical Cl atom of a second dinuclear complex [O(1)–H(2w)···Cl(3)(2 − x, ȳ, 1 − z) 3·115 (8), H(2w)···Cl(3) 2·15 (8) Å, O(1)–H(2w)···Cl(3) 153 (6)°]. There are also two contacts relevant for packing, the geometries of which satisfy the requirements for hydrogen bonds (Berkovitch-Yellin & Leiserowitz, 1984): C(4)–H(4)···O(1)(x, y − 1, z) 3·30 (1), H(4)···O(1) 2·3 (1) Å, C(4)–H(4)···O(1) 146 (9)°, and C(8)–H(8)···Cl(1)(x, ȳ − ½, z − ½) 3·50 (1), H(8)···Cl(1) 2·4 (1) Å, C(8)–H(8)···Cl(1) 165 (9)°.

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μ-Oxo-1,1,1,2,2,2-hexaoxo-1,1,2-tris(pyridine)dirhenium(VII), [Re₂O₇(C₅H₅N)₃]: Variability of the Coordination Number of Re^{VII}

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Abstract. $M_r = 721·7$, monoclinic, $P2_1/c$, $a = 9·068$ (1), $b = 12·280$ (2), $c = 17·494$ (4) Å, $\beta = 95·02$ (1)°, $Z = 4$, $D_x = 2·47$ g cm^{-3}, D_m not measured, graphite-monochromatized Mo Kα radiation, $\lambda = 0·71073$ Å, $\mu = 126·8$ cm^{-1}, $F(000) = 1320$, $T = 293$ (2) K. Final $R = 0·026$ for 1764 independent observed reflections. [Re₂O₇py₃] molecules contain two inequivalent rhenium atoms bridged by a single oxygen atom, Re(1)–O = 1·806 (7), Re(2)–O = 2·056 (7) Å. Re(1) is five-coordinate in a trigonal bipyramidal geometry with three oxo ligands [Re(1)–O = 1·695–1·706 (9) Å], the bridging oxygen atom, and a pyridine nitrogen atom in its coordination sphere. Re(2) is six-coordinate in a distorted octahedral geometry with a *fac*-trioxo group [Re(2)–O = 1·710– 1·724 (9) Å], the bridging oxygen atom, and two pyridine nitrogen atoms.

Introduction. The chemistry of oxo complexes of Re^{7+} is dominated by tetrahedral [ReO₄]$^-$. A few examples of octahedral [ReO₃X_3] units are known in Re₂O₇ (Krebs, Müller & Beyer, 1968, 1969), Re₂O₇.2H₂O (Beyer, Glemser & Krebs, 1968; Beyer, Glemser, Krebs & Wagner, 1970), [Re₂O₆(OH)₂(1,4-dioxane)₃] (Fischer & Krebs, 1982), [ReO₃Cl(2,2'-bipyridine)] (Sergienko, Khodashova, Porai-Koshits & Butman, 1977), H₂phen[ReO₃Cl₂(H₂O)]Cl (Lis, 1979) and Cs₂[ReO₃Cl₃] (Lis, 1983).

Five-coordinate Re^{7+} compounds are known. [ReO₂F₃] has been shown by matrix-isolation vibrational spectroscopy to have a trigonal bipyramidal (C_{2v}) structure with equatorial oxygen atoms (Beattie,