

Poly{aquadichloro[3,6-di(2-pyridyl)pyridazine]- μ -hydroxo-dicopper(II) Chloride Dihydrate}, $\{[\text{Cu}_2(\text{C}_{14}\text{H}_{10}\text{N}_4)\text{Cl}_2(\text{H}_2\text{O})(\text{OH})\text{Cl}]\}_n \cdot 2n\text{H}_2\text{O}$

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Abstract. M_r (dinuclear unit) = 538.764, orthorhombic, $Pbca$, $a = 22.519$ (3), $b = 23.318$ (3), $c = 7.303$ (1) Å, $V = 3834.8$ (9) Å³, $Z = 8$, D_m (by flotation) = 1.87, $D_x = 1.866$ g cm⁻³, $F(000) = 2160$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 26.75$ cm⁻¹, $T = 293$ K. The final conventional R is 0.077 over the 1528 unique observed reflections. The compound has been obtained by exposure to air, and slow evaporation, of an aqueous solution of the product of the reaction between the dinuclear complex aquatrichlorohydroxo[3,6-di(2-pyridyl)pyridazine]dicopper(II) and 0.1 M hydrazine. The asymmetric unit consists of chloride anions, solvent water molecules, and dinuclear cations joined to each other to form a polymeric array through a weak linkage between a Cu atom and a bridging hydroxy group of another dinuclear moiety. Both Cu atoms have a distorted square-pyramidal geometry.

Introduction. Within the framework of a systematic research on dinuclear complexes of transition metals with organic molecules containing nitrogen donor atoms, the title complex has been synthesized. In order to obtain further information about dinuclear structures of copper(II) a crystal structure determination was undertaken.

Experimental. Green–yellow parallelepiped crystals, 0.40 × 0.20 × 0.15 mm, Siemens–Stoe diffractometer, Mo $K\alpha$ radiation, three standard reflections, 2143 unique measured reflections with $\theta < 25^\circ$, 1528 with $I > 3\sigma(I)$, θ – 2θ scan technique, Lp correction, absorption ignored, 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); direct methods, full matrix, $\sum w(|F_o| - |F_c|)^2$ minimized, anisotropic thermal parameters for Cu, Cl, N, and O linked to metal atoms, isotropic for the other

atoms, H of the hydroxy group (from ΔF synthesis) and the other hydrogens (calculated) isotropic U of 0.04 Å² and not refined; final $R = 0.077$, $R_w = 0.057$, $w = 1/\sigma^2$; VAX/VMS computer of the Università della Calabria; SHELX program (Sheldrick, 1976) and XRAY system of programs (Stewart, Kundell & Baldwin, 1970).†

Discussion. The asymmetric unit consists of chloride anions, of solvent water molecules, and of dinuclear cations joined to each other to form a polymeric array through weak bonds [2.772 (11) Å] between a Cu atom and a bridging hydroxy group of another dinuclear unit (Fig. 1). A view of the cell is shown in Fig. 2. The final atomic parameters are reported in Table 1, selected bond distances and angles are in Table 2.

† 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 38375 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

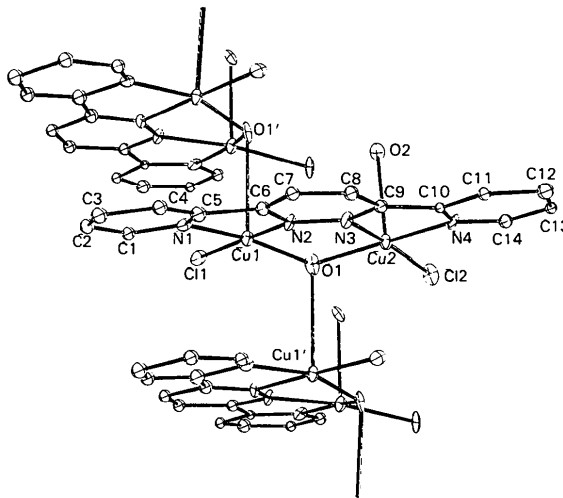


Fig. 1. View of the polymeric cation with the atomic labelling system.

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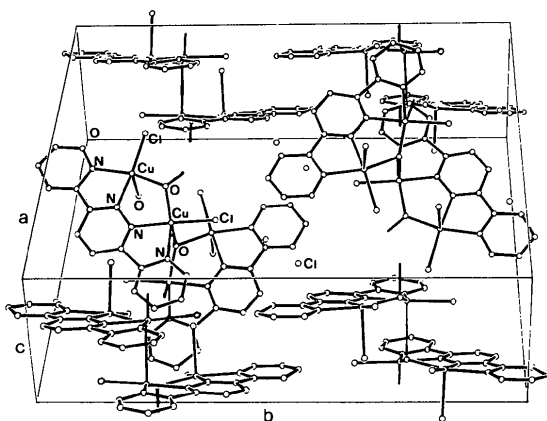


Fig. 2. Packing of the structure.

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

	x	y	z	$U_{eq}(\text{Å}^2)$
Cu(1)	1098 (1)	2431 (1)	4359 (3)	25 (1)
Cu(2)	83 (1)	3320 (1)	2451 (4)	27 (1)
Cl(1)	1030 (2)	1490 (2)	4290 (7)	32 (3)
Cl(2)	-662 (2)	3058 (2)	653 (8)	38 (3)
Cl(3)	3168 (3)	287 (2)	1127 (8)	69 (5)
O(1)	487 (4)	2570 (4)	2653 (18)	23 (7)
O(2)	-394 (4)	3275 (4)	5341 (16)	29 (8)
O(3)	3567 (5)	1019 (4)	4389 (18)	31 (3)
O(4)	-2796 (5)	5636 (5)	-2175 (21)	60 (5)
N(1)	1869 (5)	2475 (6)	5646 (19)	22 (8)
N(2)	1224 (6)	3274 (5)	4407 (20)	18 (8)
N(3)	785 (6)	3613 (5)	3756 (20)	14 (9)
N(4)	-63 (6)	4190 (5)	2345 (24)	24 (7)
C(1)	2267 (7)	2049 (7)	6086 (22)	25 (5)
C(2)	2793 (7)	2132 (7)	6836 (24)	29 (5)
C(3)	3028 (7)	2687 (6)	7018 (26)	33 (6)
C(4)	2636 (7)	3128 (7)	6519 (21)	28 (5)
C(5)	2105 (8)	3014 (8)	5831 (27)	32 (5)
C(6)	1682 (7)	3471 (6)	5211 (24)	28 (5)
C(7)	1788 (7)	4067 (6)	5339 (24)	23 (5)
C(8)	1387 (7)	4413 (6)	4655 (24)	26 (5)
C(9)	839 (7)	4188 (7)	3829 (23)	23 (5)
C(10)	387 (7)	4505 (6)	3053 (23)	14 (4)
C(11)	368 (7)	5105 (6)	3016 (24)	21 (5)
C(12)	-181 (7)	5375 (6)	2324 (29)	34 (5)
C(13)	-585 (7)	5032 (7)	1607 (25)	20 (5)
C(14)	-547 (8)	4436 (7)	1657 (25)	27 (5)

Table 2. Bond distances (Å) and angles ($^\circ$)

Cu(1)—Cl(1)	2.200 (5)	N(4)—C(10)	1.354 (21)
Cu(1)—O(1)	1.884 (11)	N(4)—C(14)	1.330 (22)
Cu(1)—N(1)	1.977 (12)	C(1)—C(2)	1.319 (23)
Cu(1)—N(2)	1.986 (12)	C(2)—C(3)	1.404 (22)
Cu(1)—O(1)'	2.772 (11)	C(3)—C(4)	1.403 (22)
Cu(2)—Cl(2)	2.216 (6)	C(4)—C(5)	1.324 (24)
Cu(2)—O(1)	1.977 (10)	C(5)—C(6)	1.499 (24)
Cu(2)—N(3)	1.968 (14)	C(6)—C(7)	1.413 (20)
Cu(2)—N(4)	2.057 (12)	C(7)—C(8)	1.310 (22)
Cu(2)—O(2)	2.370 (11)	C(8)—C(9)	1.470 (22)
N(1)—C(1)	1.376 (21)	C(9)—C(10)	1.380 (22)
N(1)—C(5)	1.371 (23)	C(10)—C(11)	1.400 (20)
N(2)—N(3)	1.352 (18)	C(11)—C(12)	1.476 (22)
N(2)—C(6)	1.273 (21)	C(12)—C(13)	1.320 (23)
N(3)—C(9)	1.347 (20)	C(13)—C(14)	1.393 (23)

Table 2 (cont.)

Cl(1)—Cu(1)—O(1)	96.1 (3)	Cu(2)—N(3)—C(9)	115.9 (11)
Cl(1)—Cu(1)—N(1)	97.1 (4)	Cu(2)—N(3)—N(2)	123.7 (9)
Cl(1)—Cu(1)—N(2)	175.8 (4)	N(2)—N(3)—C(9)	120.1 (13)
Cl(1)—Cu(1)—O(1)'	89.1 (3)	Cu(2)—N(4)—C(10)	113.6 (10)
O(1)—Cu(1)—N(1)	161.3 (5)	Cu(2)—N(4)—C(14)	124.8 (11)
O(1)—Cu(1)—N(2)	86.9 (5)	C(10)—N(4)—C(14)	121.6 (13)
O(1)—Cu(1)—O(1)'	102.2 (5)	N(1)—C(1)—C(2)	125.2 (15)
N(1)—Cu(1)—N(2)	79.3 (6)	C(1)—C(2)—C(3)	120.8 (15)
N(1)—Cu(1)—O(1)'	91.3 (5)	C(2)—C(3)—C(4)	114.4 (14)
N(2)—Cu(1)—O(1)'	93.2 (5)	C(3)—C(4)—C(5)	121.3 (16)
C(12)—Cu(2)—O(1)	98.6 (3)	C(4)—C(5)—N(1)	124.8 (17)
Cl(2)—Cu(2)—N(3)	172.1 (4)	N(1)—C(5)—C(6)	112.0 (14)
Cl(2)—Cu(2)—N(4)	97.4 (4)	C(4)—C(5)—C(6)	123.1 (16)
Cl(2)—Cu(2)—O(2)	99.9 (3)	C(5)—C(6)—N(2)	113.4 (14)
O(1)—Cu(2)—N(3)	84.3 (5)	C(5)—C(6)—C(7)	124.9 (15)
O(1)—Cu(2)—N(4)	161.6 (5)	N(2)—C(6)—C(7)	121.5 (15)
O(1)—Cu(2)—O(2)	95.9 (4)	C(6)—C(7)—C(8)	117.6 (14)
N(3)—Cu(2)—N(4)	78.7 (5)	C(7)—C(8)—C(9)	121.0 (14)
N(3)—Cu(2)—O(2)	87.0 (5)	C(8)—C(9)—C(10)	126.6 (14)
N(4)—Cu(2)—O(2)	90.3 (5)	N(3)—C(9)—C(10)	116.8 (15)
Cu(1)—O(1)—Cu(2)	122.5 (6)	C(8)—C(9)—N(3)	116.6 (14)
Cu(1)—O(1)—Cu(1)'	102.2 (6)	C(9)—C(10)—N(4)	114.7 (13)
Cu(2)—O(1)—Cu(1)'	99.5 (6)	C(9)—C(10)—C(11)	124.5 (15)
Cu(1)—N(1)—C(1)	130.2 (11)	N(4)—C(10)—C(11)	120.8 (14)
Cu(1)—N(1)—C(5)	115.8 (11)	C(10)—C(11)—C(12)	117.3 (13)
C(1)—N(1)—C(5)	112.7 (13)	C(11)—C(12)—C(13)	117.0 (14)
Cu(1)—N(2)—C(6)	118.8 (10)	C(12)—C(13)—C(14)	123.5 (16)
Cu(1)—N(2)—N(3)	117.9 (10)	C(13)—C(14)—N(4)	119.4 (16)
N(3)—N(2)—C(6)	122.9 (13)		

Both metal atoms are five-coordinated having a distorted square-pyramidal coordination geometry. However, the environments around the two metals are different, since the fifth apical position is occupied in one case by a water molecule, whereas in the other case it is occupied by the hydroxy group of another dinuclear moiety. The angles about the O atom of the hydroxy group (range 99.5 – 122.5°) are in good agreement with tetrahedral geometry. Whereas the basal plane of Cu(2) is strictly planar, that of Cu(1) deviates significantly from planarity (the deviations of the four planar atoms range between 0.011 and 0.133 Å). The displacements of the metals (both toward the apical positions, which are on the same side with respect to the basal plane) are 0.124 and 0.135 Å for Cu(1) and Cu(2), respectively. Some shorter basal distances of Cu(1) with respect to Cu(2) have been found: Cu(1)—O(1) is 1.884 (11) Å against 1.977 (10) Å found for Cu(2)—O(1), and Cu(1)—N(1) is 1.977 (12) Å against 2.057 (12) Å for Cu(2)—N(4).

The geometry of the dinuclear moiety can be compared with that found in the aquadi-chlorohydroxo[3,6-di(2-pyridyl)pyridazine]dicopper(II) complex (Manotti Lanfredi, Tiripicchio, Ghedini & De Munno, 1982), which differs from the title complex only in the different behaviour of a Cl atom which, in one case, is coordinated and, in the other, is a counter-anion, so allowing the formation of polymeric chains.

The value of the Cu...Cu separation in the dinuclear unit [3.387 (3) Å], close to the 3.376 Å value found in

the above-mentioned dicopper(II) complex, is remarkably longer than the values reported for other μ -hydroxo-dicopper(II) complexes, where values of 2.87 and 2.97 (Crawford, Richardson, Wasson, Hodgson & Hatfield, 1976) and 3.00 Å (Hoskins & Whillans, 1975) were found. This large separation is very probably due to the steric requirements of the organic ligand molecule of the title compound.

Some short contacts are found between O atoms of water molecules: O(3)···O(2) ($\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$) = 2.87 (2) Å, and between the chloride anion and another water molecule: O(4)···Cl(3) ($-x, \frac{1}{2} + y, -z - \frac{1}{2}$) = 3.11 (2) Å, and O(4)···Cl(3) ($x - \frac{1}{2}, \frac{1}{2} - y, -z$) = 3.15 (1) Å.

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Aquabis(2,2'-bipyridyl)bis(thiocyanato-*N*)calcium, $[\text{Ca}(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{SCN})_2(\text{H}_2\text{O})]$, and catena-Bis(2,2'-bipyridyl)-bis- μ -(thiocyanato-*S,N*)-barium, $[\text{Ba}(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{SCN})_2]$

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Abstract. $[\text{Ca}(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{SCN})_2(\text{H}_2\text{O})]$: $M_r = 486.6$, monoclinic, $P2_1/c$, $a = 16.33$ (1), $b = 9.851$ (3), $c = 14.802$ (7) Å, $\beta = 97.91$ (5)°, $V = 2358$ (2) Å³, $Z = 4$, $D_x = 1.370$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 0.402$ mm⁻¹, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, room temperature, $F(000) = 1008$. A block-diagonal least-squares refinement based on 1838 reflections led to R and R_w values of 7.6 and 4.8%, respectively. $[\text{Ba}(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{SCN})_2]$: $M_r = 565.86$, monoclinic, $C2/c$, $a = 17.047$ (7), $b = 10.127$ (5), $c = 14.371$ (4) Å, $\beta = 116.61$ (3)°, $V = 2218$ (2) Å³, $Z = 4$, $D_x = 1.695$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 1.933$ mm⁻¹, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, room temperature, $F(000) = 1112$. Full-matrix least-squares refinement based on 1381 reflections led to R and R_w values of 6.6 and 3.5%, respectively. The Ca²⁺ ion is seven-coordinate with the four pyridyl and two thiocyanate N atoms and one water molecule forming a distorted monocapped trigonal prism. The discrete molecules are held together by van der Waals types of interactions. The Ba²⁺ ion is eight-coordinate with six N atoms and two S atoms from thiocyanate groups of an adjacent molecule forming a distorted square antiprism.

The structure consists of long chains with thiocyanate groups bridging the Ba²⁺ ions.

Introduction. Weak interactions involving compounds normally found in biological systems have been of interest in our laboratories. We are investigating weak interactions between crown ethers and small neutral organic molecules as models for understanding secondary interactions that occur at biological receptor sites and enzyme pockets (Vögtle, Sieger & Müller 1981; Weber & Vögtle, 1981; Vögtle & Weber, 1980). These interactions may be of importance in stereoselective recognition by receptors and substrates. The coordination of alkali and alkaline-earth metals by N donors is also of interest in these studies.

Experimental. MeOH/ethyl acetate solutions of Ca(SCN)₂ and Ba(SCN)₂ were added to solutions of bipyridyl in a 1:2 ratio. The recovered Ca complex was recrystallized from acetone while the Ba complex was recrystallized from ethyl acetate. Intensity data collected on a Syntex P2₁ diffractometer system, $\theta:2\theta$ scanning technique, variable scan speed, Mo *K* α radiation, graphite monochromator. Room-temperature

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