

Synthesis and Characterization of Dinuclear Copper(II) Complexes. Crystal Structure of Aquatrchlorohydroxo-3,6-bis(2'-pyridyl)pyridazine- dicopper(II)

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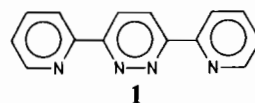
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The tetradentate ligand 3,6-bis(2'-pyridyl)pyridazine (1) forms with copper(II) chloride the dinuclear complexes Cu_2LCl_4 (2), $\text{Cu}_2\text{LCl}_3(\text{OH})\cdot\frac{1}{2}\text{H}_2\text{O}$ (3) and $\text{Cu}_2\text{LCl}_3(\text{OH})(\text{H}_2\text{O})$ (4), depending on the reaction conditions. By treatment with water, 2 and 3 transform into 4. The crystal structure of 4 has been determined by X-ray methods: it crystallizes in the triclinic space group $\text{P}\bar{1}$, with two molecules in a unit cell of dimensions $a = 10.240(7)$, $b = 11.245(9)$, $c = 8.521(6)$ Å, $\alpha = 90.0(1)$, $\beta = 114.1(1)$, $\gamma = 102.3(1)^\circ$. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares to $R = 0.053$ for 2887 observed reflections. The structure consists of dinuclear complexes, in which the copper atoms, bridged by the hydroxyl group and by the pair of nitrogen atoms of pyridazine moiety, are in a square pyramidal arrangement. Each basal coordination is completed by one pyridyl nitrogen atom from the ligand and by one chlorine atom; the apices of the pyramids are occupied by a chlorine atom and a water molecule, which, on the same side with respect to the basal coordination planes, are involved in an intramolecular hydrogen bond.

Introduction

Owing to their interesting chemical properties bimetallic complexes are receiving an increasing attention in several research fields, e.g. (i) in homogeneous catalysis, as species capable of carrying out multistep reactions or different successive processes [1]; (ii) in bioinorganic chemistry, as simple and appropriate models for naturally occurring enzymes [2]; (iii) in photochemistry, as sensitizers in energy transfer reactions [3].

Several synthetic, structural and physical studies have been performed on dinuclear copper complexes containing chelating nitrogen containing ligands [4–7]. In this context the ligand 3,6-bis(2'-pyridyl)pyridazine seemed to be interesting for its ability, when in conformation 1, to bind two



metal atoms in a very close arrangement, so providing the way for possible cooperative effects. Dinuclear copper complexes of this ligand have been prepared and the crystal structure of $\text{Cu}_2\text{LCl}_3(\text{OH})(\text{H}_2\text{O})$ has been determined by X-ray methods. A monomeric complex of the same ligand, in a different conformation with the pyridyl nitrogen atoms on opposite sides with respect to the N–N bond of the pyridazine ring, has been recently reported [8].

Experimental

Physical Measurements

Infrared spectra in nujol mull were recorded with a Perkin-Elmer 377 spectrometer. Reflectance spectra were recorded on a Beckman DK 2A instrument against MgO as reference; solution spectra were obtained with a Cary 118 spectrophotometer. Conductivity measurements were carried out with a Jones 0.1 cm cell and an LKB 5300B conductivity bridge. Thermogravimetric analyses were performed on a DTA-TG/DTG STA 429 thermal analyser. The elemental analyses were determined by the Microanalysis Laboratory of the Istituto di Farmacia dell'Università di Pisa, Pisa, Italy.

Preparation of the Ligand (1)

The ligand 3,6-bis(2'-pyridyl)pyridazine was prepared starting from 2-cyanopyridine as described in the literature [9]. *Anal.* Calcd. for $C_{14}H_{10}N_4$: C, 71.78; H, 4.30; N, 23.91. Found: C, 71.70; H, 4.34; N, 23.98.

Preparation of Cu_2LCl_4 (2)

To a solution of 1 mmol of $CuCl_2 \cdot 2H_2O$ in 30 ml of ml of acetone, 1 mmol of **1** in 20 ml of acetone was added. Stirring at room temperature for 10 min a yellow-green solid formed. The precipitate was separated by centrifugation, washed with acetone and dried under vacuum: yield 96%. *Anal.* Calcd. for $C_{14}H_{10}Cl_4Cu_2N_4$: C, 33.42; H, 2.00; N, 11.13. Found: C, 32.94; H, 1.99; N, 11.88.

Preparation of $Cu_2LCl_3(OH) \cdot \frac{1}{2}H_2O$ (3)

To a solution of 1 mmol of $CuCl_2 \cdot 2H_2O$ in 30 ml of water, 0.5 mmol of **1** in 8 ml of acetone was added. A green microcrystalline precipitate immediately formed upon stirring at room temperature. The precipitate was filtered, washed with acetone and dried: yield 90%. *Anal.* Calcd. for $C_{14}H_{11}Cl_3Cu_2N_4O \cdot \frac{1}{2}H_2O$: C, 34.06; H, 2.45; N, 11.35. Found: C, 33.99; H, 2.47; N, 11.88.

Preparation of $Cu_2LCl_3(OH)(H_2O)$ (4)

Complex **4** was obtained by slow evaporation at room temperature of a solution prepared dissolving 1 mmol of **(3)** in 30 ml of hot water. After three days large greenish blue crystals formed; they were filtered, washed with water and dried: yield 80%. *Anal.* Calcd. for $C_{14}H_{13}Cl_3Cu_2N_4O_2$: C, 33.45; H, 2.61; N, 11.14. Found: C, 33.38; H, 2.68; N, 11.13.

X-Ray Data Collection

An irregularly shaped blue crystal of **4**, having dimensions of *ca.* 0.13 × 0.16 × 0.35 mm, was used for the data collection. Preliminary cell parameters, obtained by rotation and Weissenberg photographs, were subsequently refined by least-squares from the θ values of 16 reflections accurately measured on a Siemens AED single-crystal diffractometer. The crystal data are as follows: $C_{14}H_{13}Cl_3Cu_2N_4O_2$, $M = 502.73$, triclinic, $a = 10.240(7)$, $b = 11.245(9)$, $c = 8.521(6)$ Å, $\alpha = 90.0(1)$, $\beta = 114.1(1)$, $\gamma = 102.3(1)^\circ$, $V = 871(1)$ Å³, $Z = 2$, $D_c = 1.92$ g cm⁻³, Cu-K α radiation ($\lambda = 1.54178$ Å), $\mu(Cu-K\alpha) = 74.86$ cm⁻¹, space group $P\bar{1}$ (from structure determination).

A complete set of intensity data was collected within the angular range $\theta \leq 70^\circ$. The $\theta/2\theta$ scan technique was used; a standard reflection was re-measured after every 20 reflections as a check on crystal and instrument stability (no significant change in the measured intensities of these reflections was observed during data collection). A total of 3320

TABLE I. Fractional Atomic Coordinates ($\times 10^4$) of the Non-Hydrogen Atoms with e.s.d.s in Parentheses.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
CU1	3413(1)	2225(1)	1304(1)
CU2	908(1)	3304(1)	2146(1)
CL1	1572(3)	4316(2)	4691(3)
CL2	5659(2)	2380(3)	3282(3)
CL3	-575(2)	1093(2)	2083(3)
O1	2768(7)	2938(6)	2778(8)
O _w	2132(8)	291(6)	1599(9)
N1	1567(7)	2454(6)	-617(8)
N2	595(7)	2898(6)	-290(8)
N3	-1022(8)	3776(6)	781(9)
N4	3687(7)	1693(6)	-774(9)
C1	1316(8)	2098(7)	-2225(10)
C2	10(9)	2163(8)	-3621(11)
C3	-981(10)	2656(8)	-3268(11)
C4	-650(8)	3016(7)	-1562(10)
C5	-1577(9)	3553(7)	-946(11)
C6	-2887(10)	3806(9)	-2046(13)
C7	-3679(11)	4299(10)	-1303(15)
C8	-3132(12)	4494(10)	453(15)
C9	-1799(12)	4236(9)	1476(15)
C10	2551(8)	1665(7)	-2324(10)
C11	2559(10)	1299(8)	-3832(11)
C12	3784(11)	914(9)	-3812(13)
C13	4933(11)	939(9)	-2229(13)
C14	4868(10)	1334(8)	-758(12)

independent reflections were measured, of which 2887 were considered observed and employed in the analysis, having $I \geq 2\sigma(I)$. The structure amplitudes were obtained after the usual Lorentz and polarization corrections. No correction for absorption was applied. The absolute scale and the mean temperature factor were established by Wilson's method.

Solution and Refinement of the Structure

Initial coordinates of the heavy atoms were determined by a Patterson map. A Fourier synthesis, calculated with phases of these atoms, revealed the positions of all other non-hydrogen atoms. Refinement was carried out by full-matrix least-squares, using the SHELX system of computer programs [10], first isotropically and then anisotropically. At this stage a ΔF synthesis revealed the positions of all the hydrogen atoms, which were refined isotropically. The final R value was 0.053 (observed reflections only). The function minimized in the least-squares calculations was $\sum w|\Delta F|^2$; unit weights were chosen at each stage of the refinement after analyzing the variation of $|\Delta F|$ with respect to F_o . The atomic scattering factors (corrected for anomalous dispersion of Cu and Cl) were taken from International Tables [11]. The final coordinates for the non-hydrogen and hydrogen atoms are given in Tables I

TABLE II. Fractional Coordinates ($\times 10^3$) and Isotropic Thermal Parameters ($\times 10^3$) of the Hydrogen Atoms with e.s.d.'s in Parentheses.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i>
H1	352(11)	338(9)	360(13)	52(27)
H(1) _w	140(10)	36(8)	163(11)	45(22)
H(2) _w	156(10)	-7(8)	66(12)	59(22)
H2	-22(9)	184(8)	-492(11)	63(23)
H3	-194(10)	252(8)	-404(12)	73(24)
H6	-329(10)	363(9)	-343(12)	71(26)
H7	-471(12)	452(10)	-211(13)	110(31)
H8	-371(12)	467(10)	97(14)	87(31)
H9	-137(12)	441(9)	286(14)	97(31)
H11	163(10)	130(8)	-504(12)	72(25)
H12	402(10)	91(9)	-501(13)	74(27)
H13	591(11)	64(9)	-216(12)	104(27)
H14	568(10)	133(8)	31(12)	66(25)

and II respectively. Anisotropic thermal parameters are listed in Table III. A list of observed and calculated structure factors is available from the authors on request.

All calculations were performed on the CYBER 7600 of the Centro di Calcolo Elettronico Inter-

universitario dell'Italia Nord-Orientale, Bologna, with financial support from the University of Parma.

Results and Discussion

Synthesis and Characterization of the Complexes

Reaction of *I* with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in acetone affords a yellow-green precipitate of Cu_2LCl_4 (**2**). The same reaction in acetone-water (1:1) solution immediately gives the green microcrystalline complex $\text{Cu}_2\text{LCl}_3(\text{OH}) \cdot \frac{1}{2}\text{H}_2\text{O}$ (**3**). Recrystallization of **3** from water produces well-formed greenish-blue crystals of $\text{Cu}_2\text{LCl}_3(\text{OH})(\text{H}_2\text{O})$ (**4**). All the complexes are soluble in water, slightly soluble in methanol, but are insoluble in common organic solvents. Infrared data and selected physical properties for compounds 1-4 are reported in Table IV.

Infrared data show that after coordination both the ring characteristic 991 cm^{-1} pyridine band [12] and the pyridazine 1563 and 1580 cm^{-1} bands [13] are shifted to higher wavenumbers, viz. to 1020 - 1030 cm^{-1} and 1595 - 1600 cm^{-1} respectively. The absorptions in the 3600 and 900 cm^{-1} regions for complexes **3** and **4** are attributable to the bridging OH group [14].

TABLE III. Anisotropic Thermal Parameters ($\times 10^4$) of the Non-Hydrogen Atoms with e.s.d.'s in Parentheses. Parameters are in the form: $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12})]$.

	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
CU1	251(6)	335(7)	223(6)	-12(5)	42(5)	80(5)
CU2	393(7)	331(7)	244(6)	-17(5)	133(5)	129(5)
CL1	678(16)	422(13)	354(12)	-101(9)	258(11)	79(11)
CL2	277(11)	933(21)	368(13)	-118(13)	-46(9)	134(12)
CL3	440(12)	333(11)	322(11)	-39(8)	148(9)	7(9)
O1	355(35)	470(37)	259(31)	-66(27)	49(27)	129(30)
O _w	382(38)	451(37)	354(36)	-67(28)	79(30)	126(30)
N1	274(33)	306(35)	212(32)	-6(26)	89(27)	105(27)
N2	279(34)	304(35)	277(35)	21(27)	122(28)	114(28)
N3	399(40)	341(38)	339(39)	-14(30)	197(32)	134(31)
N4	241(33)	321(36)	308(36)	27(28)	79(28)	94(28)
C1	257(38)	308(41)	229(38)	-8(31)	111(31)	80(31)
C2	320(43)	456(49)	216(42)	2(35)	94(35)	125(37)
C3	258(44)	507(53)	267(43)	13(37)	65(36)	134(39)
C4	243(38)	327(42)	247(40)	2(32)	89(32)	89(32)
C5	328(43)	326(43)	338(45)	13(34)	192(36)	113(35)
C6	326(46)	458(54)	507(60)	79(44)	199(43)	153(40)
C7	411(54)	502(60)	678(74)	72(52)	274(53)	226(47)
C8	511(60)	534(60)	673(72)	49(51)	380(55)	236(49)
C9	532(59)	449(54)	506(69)	14(47)	296(54)	177(45)
C10	288(39)	301(41)	266(40)	20(32)	138(33)	102(32)
C11	412(52)	481(52)	273(46)	23(38)	135(40)	214(42)
C12	524(57)	526(57)	412(54)	79(43)	247(46)	282(46)
C13	406(53)	466(53)	548(58)	63(43)	237(46)	230(43)
C14	313(46)	417(49)	382(52)	59(39)	131(41)	171(38)

TABLE IV. Physical Properties of the Compounds.

No.	Compound	Infrared Spectra ^a				Electronic Spectra ^b		Conductivity ^e $\Omega^{-1} \text{ mole}^{-1} \text{ cm}^{-2}$
		O—H cm^{-1}	H ₂ O cm^{-1}	Pyridazine cm^{-1}	Pyridine cm^{-1}	Reflectance KK	Solution ^c KK; $\epsilon \text{ mole}^{-1} \text{ cm}^{-1}$	
1	C ₁₄ H ₁₀ N ₄ (L)			1580(m) 1563(m)	991(m)			
2	Cu ₂ LCl ₄			1600(m)	1040(m) 1020(m)	(23.8)	(23.5); ϵ , 129 ^d 15.75; ϵ , 77	560 ^f
3	Cu ₂ LCl ₃ (OH)·½H ₂ O	3620(w) 930(m)	3390(w) ^g 912(m)	1598(m)	1040(m) 1021(m)	(21.3)	15.75; ϵ , 76	350
4	Cu ₂ LCl ₃ (OH)(H ₂ O)	3630(w) 930(m)	3385(w) ^g 3310(w) ^g 924(m) 916(m)	1595(m)	1040(m) 1022(m)	(22.2)	15.75; ϵ , 76	353

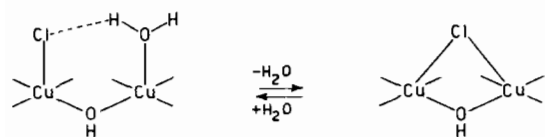
^aAs nujol mull. ^bShoulders are in parentheses. ^cIn water. ^dFreshly prepared solution. After several hours the shoulder disappears and the spectrum exhibits only a max. at 15.75, ϵ 75. After several hours the value reaches 620. ^eBroad.

^fFreshly prepared solution. ^gIn water 10⁻⁴ M at 25 °C.

The X-ray structure of 4 (see below) shows two pentacoordinated copper atoms in a square pyramidal arrangement, each copper being coordinated to two nitrogen atoms from a pyridyl and the pyridazine ring of 1, to a bridging hydroxyl group, and to a chlorine atom. The two apices of the pyramids are occupied by a chlorine atom and a water molecule, on the same side with respect to the basal plane.

Thermogravimetric analysis (T.G.A.) of 4 shows the loss of one equivalent of water at 90 °C, while 3 loses a half equivalent of water at 100 °C. The two samples after T.G.A. exhibit the same infrared spectrum containing a single 930 cm^{-1} band, besides the 3620 cm^{-1} absorption. Infrared spectra (Table IV) of 3 and 4 in the 910–925 and 3400 cm^{-1} regions show different patterns which suggest that in complex 3 water is not coordinated to the metal. It is also noteworthy that compound 3 goes to 4 by recrystallization from water.

In dinuclear copper complexes having a stoichiometry Cu₂LCl₃(OH) with ligands closely related to 1, a symmetrical arrangement around the two copper atoms has been found, with a chlorine bridge in addition to the hydroxyl bridge [2]. On the basis of the previous considerations we can therefore suppose in 3 the presence of a chlorine bridge, that forms when water is lost from 4, as depicted below:



The complexes 2–4 have quite similar reflectance spectra (Table IV), the different position of the

maximum of complex 2 being attributable to the presence of a different chromophore. By reaction with silver nitrate 3 and 4 give three equivalents of silver chloride and 2 gives four, in agreement with their halogen content. The mobility of all the halogen ions, together with conductivity data for similar complexes such as Cu₂LX₃(OH) (X = Cl, Br, IO₃; L = 1,4-di(2'-pyridyl)aminophthalazine), has been reported [5] in a suggestion that the actual species predominant in solution is the aquated cation Cu₂L(OH)(H₂O)₃³⁺. This could be also the situation for complexes 2–4 in aqueous solution. Actually 2 has a conductivity value higher than 3 and 4 (Table IV) and this value increases with time as well as the pH of the solution; moreover, while 3 and 4 exhibit identical electronic spectra with the maximum at 15.75 kk, the complex 2 has in addition to this maximum a shoulder at 23.5 kk that disappears after a few hours.

These observations seem to support the fact that 2 could transform into the same aquated cation generated by 3 and 4, by a way that involves the formation of hydrochloric acid with a hydrolysis reaction whose final tail only has been observed. This view is supported by the fact that none of the synthesized complexes is E.P.R. active in water at 77 K, suggesting that the actual aquated species all contain a μ -bridging OH group that could be responsible for an antiferromagnetic coupling, as observed for similar dicopper compounds [15].

Description of the Structure of 4

The crystal structure of 4 consists of dinuclear [Cu₂(C₁₄H₁₀N₄)Cl₃(OH)(H₂O)] complexes (Fig. 1), containing pentacoordinated copper atoms bridged by the hydroxyl group and the pair of nitrogen

TABLE V. Bond Distances (Å) and Angles (°).

a) In the coordination polyhedra			
Cu(1)–O(1)	1.887(7)	Cu(2)–O(1)	1.893(7)
Cu(1)–N(1)	2.000(7)	Cu(2)–N(2)	2.004(6)
Cu(1)–N(4)	2.012(7)	Cu(2)–N(3)	2.027(8)
Cu(1)–Cl(2)	2.196(3)	Cu(2)–Cl(1)	2.220(3)
Cu(1)–O _w	2.359(8)	Cu(2)–Cl(3)	2.611(3)
O(1)–Cu(1)–Cl(2)	94.9(2)	O(1)–Cu(2)–Cl(1)	93.3(2)
O(1)–Cu(1)–N(1)	85.7(3)	O(1)–Cu(2)–N(2)	85.4(3)
N(1)–Cu(1)–N(4)	78.8(3)	N(2)–Cu(2)–N(3)	78.3(3)
N(4)–Cu(1)–Cl(2)	99.0(2)	N(3)–Cu(2)–Cl(1)	100.1(2)
O(1)–Cu(1)–N(4)	163.6(3)	O(1)–Cu(2)–N(3)	162.4(3)
N(1)–Cu(1)–Cl(2)	167.0(2)	N(2)–Cu(2)–Cl(1)	162.3(2)
O _w –Cu(1)–O(1)	88.8(3)	Cl(3)–Cu(2)–O(1)	95.7(2)
O _w –Cu(1)–Cl(2)	103.3(2)	Cl(3)–Cu(2)–Cl(1)	109.0(1)
O _w –Cu(1)–N(1)	89.7(3)	Cl(3)–Cu(2)–N(2)	88.7(2)
O _w –Cu(1)–N(4)	96.4(3)	Cl(3)–Cu(2)–N(3)	88.9(2)
b) in the organic ligand			
N(1)–N(2)	1.325(9)	C(8)–C(9)	1.380(14)
N(1)–C(1)	1.331(10)	C(9)–N(3)	1.346(14)
C(1)–C(2)	1.397(12)	N(3)–C(5)	1.345(11)
C(2)–C(3)	1.384(13)	C(1)–C(10)	1.481(12)
C(3)–C(4)	1.390(12)	C(10)–C(11)	1.353(12)
C(4)–N(2)	1.327(11)	C(11)–C(12)	1.405(14)
C(4)–C(5)	1.481(12)	C(12)–C(13)	1.376(14)
C(5)–C(6)	1.377(13)	C(13)–C(14)	1.362(14)
C(6)–C(7)	1.406(14)	C(14)–N(4)	1.349(13)
C(7)–C(8)	1.365(14)	N(4)–C(10)	1.352(11)
C(2)–H(2)	1.08(9)	C(9)–H(9)	1.08(10)
C(3)–H(3)	0.91(10)	C(11)–H(11)	1.08(9)
C(6)–H(6)	1.08(9)	C(12)–H(12)	1.14(10)
C(7)–H(7)	1.08(11)	C(13)–H(13)	1.10(11)
C(8)–H(8)	0.92(12)	C(14)–H(14)	0.95(10)
N(2)–N(1)–C(1)	121.1(7)	C(7)–C(8)–C(9)	120.0(10)
N(1)–C(1)–C(2)	121.1(8)	C(8)–C(9)–N(3)	121.4(10)
C(1)–C(2)–C(3)	117.2(8)	C(9)–N(3)–C(5)	118.7(9)
C(2)–C(3)–C(4)	118.8(8)	N(1)–C(1)–C(10)	112.8(7)
C(3)–C(4)–N(2)	120.9(8)	C(2)–C(1)–C(10)	126.0(7)
C(3)–C(4)–C(5)	126.2(8)	C(1)–C(10)–N(4)	114.0(7)
C(5)–C(4)–N(2)	112.9(7)	C(1)–C(10)–C(11)	123.1(8)
C(4)–N(2)–N(1)	120.8(7)	N(4)–C(10)–C(11)	122.9(8)
C(4)–C(5)–C(6)	122.9(8)	C(10)–C(11)–C(12)	119.4(9)
C(4)–C(5)–N(3)	114.0(8)	C(11)–C(12)–C(13)	117.4(9)
N(3)–C(5)–C(6)	123.1(9)	C(12)–C(13)–C(14)	120.4(10)
C(5)–C(6)–C(7)	117.6(9)	C(13)–C(14)–N(4)	122.3(9)
C(6)–C(7)–C(8)	119.2(9)	C(14)–N(4)–C(10)	117.6(7)
Cu(1)–N(1)–N(2)	120.9(5)	Cu(2)–N(2)–N(1)	120.7(5)
c) in the water molecule and hydroxyl group			
O _w –H(1) _w	0.78(10)	O(1)–H(1)	0.85(10)
O _w –H(2) _w	0.81(9)		
H(1) _w –O _w –H(2) _w	82(6)	Cu(1)–O(1)–H(1)	108(6)
Cu(1)–O(1)–Cu(2)	126.5(3)	Cu(2)–O(1)–H(1)	119(6)
d) hydrogen bonds			
O _w –H(1) _w ···Cl(3)	3.266(8)	O _w –H(1) _w –Cl(3)	166(7)

(continued overleaf)

TABLE V. (continued)

$H(1)_w \cdots Cl(3)$	2.50(9)	$H(1)_w - O_w - Cl(3)$	11(5)
$O_w - H(2)_w \cdots Cl(3^i)$	3.109(7)	$O_w - H(2)_w - Cl(3^i)$	163(6)
$H(2)_w \cdots Cl(3^i)$	2.32(9)	$H(2)_w - O_w - Cl(3^i)$	13(5)

Asymmetric units:

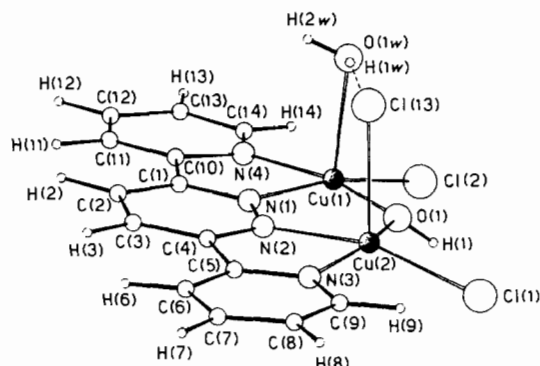
i $-x, -y, -z$ 

Fig. 1. View of the molecular shape of the dinuclear complex $Cu_2(C_{14}H_{10}N_4)Cl_3(OH)(H_2O)$ with the atomic numbering system.

atoms of the pyridazine ring of the tetranitrogenated ligand. Bond distances and angles in the complex are given in Table V. The environment of both copper atoms is square pyramidal with the apices on the same side with respect to the basal coordination planes. For each copper atom the basal coordinated atoms are one pyridyl nitrogen atom of the ligand, one of the pair of the nitrogens of the pyridazine moiety, a chlorine atom and the oxygen atom of the bridging hydroxyl group. The apices of the two pyramids are occupied by an oxygen of the water molecule and by the third chlorine atom. The copper atoms Cu(1) and Cu(2) are displaced from the mean planes passing through the basal atoms of 0.187 and 0.256 Å respectively, towards the corresponding O_w and Cl(3) apical atoms. The Cu(1)– O_w and Cu(2)–Cl(3) directions make angles of 8.9 and 12.3° respectively with the normal to the corresponding basal plane. The dihedral angle between the two basal planes, sharing a corner (hydroxy bridge), is 7.6°.

The Cu···Cu separation (3.376 Å), much longer than those of 2.78–3.00 Å found in di- μ -hydroxo-dicopper(II) [15, 16], agrees well with the mean value of 3.23 Å found in the closely related trichloro-hydroxo-1,4-di(2'-pyridyl)aminophthalazine-dicopper(II) sesquihydrate [6]. A comparison of the structural features of the coordination polyhedra around the bridged copper atoms in this last complex

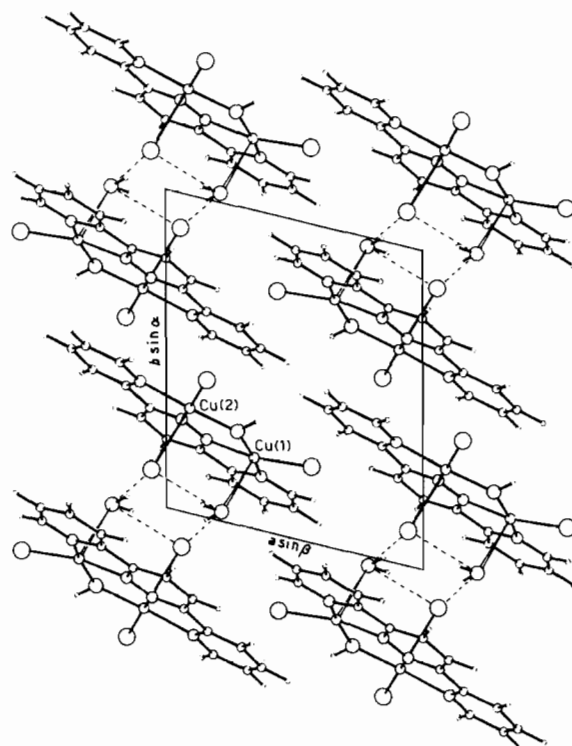


Fig. 2. Projection of the structure along c showing the packing of the complexes.

with those of the present complex shows that the main differences concern the bond angles involving the hydroxy bridge, probably because the square pyramids around the metal atoms share one corner (hydroxy bridge) in the present complex and share both a corner (hydroxy bridge) and the apex (bridging chlorine) in the other complex.

The Cu–N bonds in the present complex are comparable with the equatorial Cu–N bonds found in the mononuclear complex formed by the same ligand in chloro-bis(3,6-bis(2'-pyridyl)pyridazine)-copper(II) chloride pentahydrate [8], with the metal atom in a trigonal bipyramidal arrangement. The organic ligand, having the pyridyl nitrogen atoms on the same side (with respect to the N–N bond of the pyridazine moiety) in a manner different from that seen in the mononuclear complex, is roughly planar (the maximum displacement from the mean plane

being 0.11 Å for C(7)). The two pyridyl groups are twisted with respect to the pyridazine moiety, about the exocyclic C–C bonds, by 3.3 and 3.0° for the groups defined by N(3) and N(4) respectively.

The bond distances and angles in the ligand are quite regular and are in good agreement with those reported in the mononuclear complex of the same ligand.

The apical chlorine atom is involved in an intramolecular hydrogen bond with the water molecule of the same complex, and also in an intermolecular hydrogen bond with the water molecule of an adjacent complex, related by the symmetry center at 0, 0, 0. This latter intermolecular hydrogen bond joins the complexes in dimers (Fig. 2). C–H···Cl interactions seem to play a significant role in determining the packing of the dimers. The geometries of these interactions satisfy the requirements for C–H···Cl hydrogen bonds [H(3)···Cl(2) ($-1 + x, y, -1 + z$) = 2.56 Å, C(3)–H(3)–Cl(2) ($-1 + x, y, -1 + z$) = 165°; H(2)···Cl(3) ($x, y, -1 + z$) = 2.54 Å, C(2)–H(2)–Cl(3) ($x, y, -1 + z$) = 176°; H(11)···Cl(3) ($x, y, -1 + z$) = 2.53 Å, H(11)–C(11)–Cl(3) ($x, y, -1 + z$) = 175°].

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