

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

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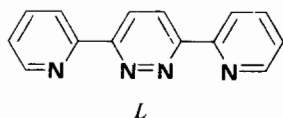
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Copper(II) chloride reacts, in appropriate conditions, with the tetradentate ligand 3,6-bis(2'-pyridyl)pyridazine yielding the dinuclear complex  $[\text{Cu}_2\text{LCl}_4(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ , whose crystal structure has been determined by X-ray methods. It crystallizes in the triclinic space group  $P\bar{1}$ , with two molecules in a unit cell of dimensions  $a = 11.685(6)$ ,  $b = 10.003(6)$ ,  $c = 8.570(5)$  Å,  $\alpha = 66.94(8)$ ,  $\beta = 78.86(8)$ ,  $\gamma = 83.07(8)^\circ$ . The structure has been solved by Patterson and Fourier methods and refinement by full-matrix least-squares to  $R = 0.068$  for 1513 observed reflections. The structure is strictly related to that reported [1] for the complex  $[\text{Cu}_2\text{LCl}_3(\text{OH})(\text{H}_2\text{O})]$ , the main difference being the longer  $\text{Cu} \cdots \text{Cu}$  separation which is dependent on the different bridging group (Cl instead of OH). The facility of L to undergo large distortions is emphasized. The reactivity of the title complex with water and nitric acid is also discussed.

### Introduction

In a previous paper [1] we showed that the tetradentate ligand 3,6-bis(2'-pyridyl)pyridazine (L) is able to bind two copper(II) atoms affording an arrangement suitable for cooperative effects between the metal centers:



Thus the preparation of the dinuclear complexes  $[\text{Cu}_2\text{LCl}_4]$  (1),  $[\text{Cu}_2\text{LCl}_3(\text{OH})]$  (2) and  $[\text{Cu}_2\text{LCl}_3$

$(\text{OH})(\text{H}_2\text{O})]$  (3) was reported and the crystal structure of 3 determined and discussed.

It seemed interesting to obtain analogous binuclear complexes containing bridging groups different from OH, in order to study the changes in their structural features concerning, in particular, the  $\text{Cu} \cdots \text{Cu}$  separation. Accordingly, in this paper we describe the synthesis and the characterization of the new compounds  $[\text{Cu}_2\text{LCl}_4(\text{H}_2\text{O})]$  (4) and  $[\text{Cu}_2\text{LCl}_3(\text{NO}_3)]$  (5). The crystal structure of 4 is determined and discussed following the premise.

### Experimental

Infrared spectra were recorded as nujol mulls with a Perkin-Elmer 377 spectrophotometer. Reflectance spectra were obtained using a Beckmann DK 2A instrument against MgO as reference; electronic spectra in solution were recorded with a Cary 118 C spectrophotometer. The elemental analyses were determined by the Microanalysis Laboratory of the Istituto di Chimica Organica, Facoltà di Farmacia, Università di Pisa, Pisa (Italy). The ligand was prepared as described in the literature [2].

#### Preparation of $[\text{Cu}_2\text{LCl}_4(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ (4)

To a stirred solution of 2 mmol of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in 5 ml of water, 1 mmol of L in 20 ml of acetone was added at room temperature. The yellow-green microcrystalline precipitate that formed immediately was recovered on filtration, washed with acetone and dried in the air: yield 93%. *Anal.* Calcd. for  $\text{C}_{14}\text{H}_{14}\text{Cl}_4\text{Cu}_2\text{N}_4\text{O}_2$ : C, 31.19; H, 2.62; N, 10.43. Found: C, 31.75; H, 2.73; N, 10.89.

TABLE I. Positional Parameters ( $\times 10^4$ ) and Anisotropic Temperature Factors ( $\times 10^4$ ) in the Form:  $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}) + \dots]$ .

	x/a	y/b	z/c	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
Cu(1)	2796(2)	2781(2)	-238(2)	563(13)	691(15)	294(11)	115(10)	-146(9)	-80(10)
Cu(2)	1721(2)	-250(2)	-482(2)	503(12)	909(16)	315(11)	196(10)	-247(9)	-264(11)
Cl(1)	2583(4)	5021(4)	-1996(5)	1200(39)	534(28)	507(28)	163(26)	-392(27)	-10(22)
Cl(2)	3880(3)	-1030(4)	-1463(4)	397(20)	751(28)	352(21)	94(19)	-148(17)	-264(20)
Cl(3)	687(4)	-126(7)	-2452(6)	615(29)	2464(60)	696(32)	515(33)	-451(25)	-937(38)
Cl(4)	1842(5)	2048(7)	-1680(8)	1136(46)	1319(50)	841(41)	56(38)	-240(35)	-331(37)
O(1)	4612(8)	1955(10)	-1424(13)	581(66)	568(69)	632(71)	12(53)	-171(55)	-137(56)
N(1)	3418(9)	3259(11)	1564(12)	359(64)	328(69)	215(59)	61(52)	-72(49)	-36(51)
N(2)	2657(8)	826(11)	1743(12)	330(60)	412(70)	143(56)	-57(51)	-100(46)	-10(50)
N(3)	2247(9)	-285(12)	1679(12)	383(62)	341(69)	190(59)	73(52)	-133(49)	-131(52)
N(4)	1406(9)	-2301(13)	1100(15)	307(61)	782(92)	561(81)	6(59)	-93(58)	-452(73)

The product was insoluble in the usual organic solvents and slightly soluble in aqueous media. Suitable crystals for X-ray measurements were obtained by dissolving the microcrystalline material in a refluxing aqueous solution of 0.1 M HCl and slowly evaporating the solution, at room temperature, to a small volume (2–3 days). The nature of the compound was checked by elemental analysis and I.R. From neutral or less acidic solutions, instead of **4**, a mixture of crystals of **2** and **3** (characterized by I.R. and electronic spectrophotometry) was recovered.

#### Preparation of $[\text{Cu}_2\text{LCl}_3(\text{NO}_3)] \cdot \text{H}_2\text{O}$ (**5**)

Complex **5** was obtained as green crystals, in quantitative yield, by slow evaporation at room temperature of a solution prepared dissolving 1 mmol of **4** in hot 0.1 M nitric acid. *Anal.* Calcd. for  $\text{C}_{14}\text{H}_{14}\text{Cl}_3\text{Cu}_2\text{N}_5\text{O}_4$ : C, 30.84; H, 2.57; N, 12.74. Found: C, 31.38; H, 2.30; N, 12.66.

#### Crystal Data and Data Collection

The crystal of complex **4** used for the data collection was a parallelepiped having dimensions 0.40  $\times$  0.15  $\times$  0.10 mm. Unit cell parameters were determined by accurately measuring the setting angles of 25 reflections at room-temperature (*ca.* 22 °C) on a Philips PW 1100 diffractometer. The crystal data are as follows:  $\text{C}_{14}\text{H}_{14}\text{Cl}_4\text{Cu}_2\text{N}_4\text{O}_2$ ,  $M = 539.19$ , triclinic,  $P\bar{1}$ ,  $a = 11.685(6)$ ,  $b = 10.003(6)$ ,  $c = 8.570(5)$  Å,  $\alpha = 66.94(8)$ ,  $\beta = 79.86(8)$ ,  $\gamma = 83.07(8)^\circ$ ,  $V = 905.8$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.98$  g cm<sup>-3</sup>,  $\lambda(\text{Mo-K}\alpha) = 0.70926$  Å,  $\mu(\text{Mo-K}\alpha) = 28.2$  cm<sup>-1</sup>.

The intensity data of the reflections with  $5^\circ \leq 2\theta \leq 50^\circ$  were obtained using the  $\omega$ - $2\theta$  scan technique with a scan speed of 0.08° s<sup>-1</sup> in a variable range of (0.80 + 0.30 tg  $\omega$ )° across the peak. Three standard reflections were measured every 120 min during the data collection, but no significant varia-

tion was noticed. The intensity data were corrected for Lorentz and polarization effects; the standard deviations  $\sigma(i)$  were estimated as described elsewhere [3] with an instability factor of 0.03. A reflection was considered unobserved if its net intensity  $I$  was  $< 3\sigma(I)$ ; 1513 reflections, out of the measured 3186, had intensities  $\geq 3\sigma(I)$ . A correction for absorption was applied by using a numerical method. Atomic scattering factors were taken from Refs. 4 and 5 for non-hydrogen and hydrogen atoms respectively. Corrections for anomalous dispersion effects were also applied [6].

#### Solution and Refinement of the Structure

A three-dimensional Patterson synthesis yielded the positional parameters of the copper atoms. Successive  $F_o$  Fourier syntheses showed the positions of non-hydrogen atoms. The structure was refined by means of full-matrix least-squares of the SHELX 76 computer program [7], the minimized function being  $\sum w(|F_o| - |F_c|)^2$ , where  $w$  is the weight assigned to the  $F_o$  values according to the expression  $w = 1/\sigma^2(F_o)$ .

The hydrogen atoms of the ligand molecule were introduced in calculated positions, with an overall temperature factor  $U$  of 0.04 Å<sup>2</sup> and were not refined. These positions were varied at each cycle on the basis of the shift of the carbon atoms, keeping the C–H distance fixed at 1.08 Å. The positions of the hydrogen atoms H(1)<sub>w</sub> and H(2)<sub>w</sub>, belonging to the water molecule linked to a copper atom, were found by a  $\Delta F$  Fourier map. For copper, chlorine, nitrogen and oxygen (O<sub>1</sub>) atoms anisotropic temperature factors were used; to the other atoms isotropic temperature factors were assigned.

The final conventional R factor was 0.068. The  $R_w$ , defined as  $[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ , was

TABLE II. Positional Parameters ( $\times 10^4$ ) and Isotropic Temperature Factors ( $\times 10^4$ ).

	x/a	y/b	z/c	U
C <sub>1</sub>	3808(11)	4514(16)	1362(18)	375(34)
C <sub>2</sub>	4212(13)	4688(17)	2631(20)	577(43)
C <sub>3</sub>	4216(12)	3529(15)	4178(19)	514(39)
C <sub>4</sub>	3823(12)	2248(16)	4394(20)	524(42)
C <sub>5</sub>	3443(10)	2104(14)	3042(17)	339(33)
C <sub>6</sub>	3037(11)	769(14)	3166(17)	360(33)
C <sub>7</sub>	2974(11)	-551(14)	4556(17)	396(34)
C <sub>8</sub>	2564(12)	-1706(16)	4502(19)	445(39)
C <sub>9</sub>	2172(10)	-1545(14)	2942(17)	352(33)
C <sub>10</sub>	1715(12)	-2680(15)	2659(19)	411(37)
C <sub>11</sub>	1542(12)	-4043(16)	3825(20)	580(42)
C <sub>12</sub>	1095(13)	-5110(18)	3505(21)	560(44)
C <sub>13</sub>	831(14)	-4633(18)	1922(22)	681(50)
C <sub>14</sub>	979(13)	-3315(17)	753(22)	596(42)
O <sub>2</sub>	-373(21)	-1921(26)	-3937(34)	2165(100)
H				
H <sub>1W</sub> <sup>a</sup>	0.449	0.107	-0.150	
H <sub>2W</sub> <sup>a</sup>	0.569	0.211	-0.171	

<sup>a</sup>From  $\Delta F$  synthesis.

0.069. A final  $\Delta F$  Fourier synthesis did not show unusual features. The final values of the parameters are reported in Tables I and II. A list of observed and calculated structure factors is available from the authors on request.

## Results and Discussion

### Synthesis, Characterization and Reactivity of the Complexes

Reaction of *L* with  $\text{CuCl}_2 \cdot \text{H}_2\text{O}$  in water–acetone solution (1:4) immediately yields a yellow-green precipitate of  $\text{Cu}_2\text{LCl}_4(\text{H}_2\text{O}) \cdot \text{H}_2\text{O}$  (*4*). Due to its very low solubility in organic solvents, this complex must be recrystallized from aqueous solutions, but the operation is effective only if a substantial concentration of hydrochloric acid (not less than 0.1 *M*) is present. Using lower concentrations gives rise to the substitution of the bridging chlorine atom for a bridging hydroxo group, and to the subsequent formation of *2* and *3* by crystallization. It is noteworthy that the reaction between *L* and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  affords as unique products either the complex  $\text{Cu}_2\text{LCl}_3(\text{OH}) \cdot \frac{1}{2}\text{H}_2\text{O}$  strictly related to *3*, or the complex  $\text{Cu}_2\text{LCl}_4$  (*2*) when the reaction is carried out in 3:1 water–acetone or acetone alone, respectively [1]. Furthermore, when crystallized from solutions of 0.1 *M* nitric acid, complex *4* undergoes the substitution of a chlorine for a nitrate ion and the formation of complex  $\text{Cu}_2\text{LCl}_3(\text{NO}_3) \cdot \text{H}_2\text{O}$  (*5*). Both *4* and *5* can be prepared by crystallization of *3* from aqueous solutions containing 0.1 *M* HCl or 0.1 *M* HNO<sub>3</sub> respectively.

Spectroscopic data of *4* and *5* are reported in Table III; those of *L* and *3* are given for comparison.

The chemical behaviour of complexes *2*–*5* indicates that the concentrations of both the hydrogen and the ligating ions are critical with respect to the nature of the compound actually recovered from the aqueous solutions, thus supporting the hypothesis that the common intermediate species actually present in solution could be the aquated cation

TABLE III. Spectroscopic Data of the Compounds.

Compound	Infrared Spectra <sup>a</sup> ( $\text{cm}^{-1}$ )			Electronic Spectra <sup>b</sup> ( $\text{kK}$ ; $\epsilon$ , $\text{mol}^{-1} \text{cm}^{-1}$ )	
	H <sub>2</sub> O	Pyridazine	Pyridine	Reflectance	Solution <sup>c</sup>
<i>L</i> C <sub>14</sub> H <sub>10</sub> N <sub>4</sub>		1580(m) 1563(m)	991(m)		
<i>3</i> Cu <sub>2</sub> LCl <sub>3</sub> (OH)(H <sub>2</sub> O)	3385 <sup>d</sup> (w) 3310 <sup>d</sup> (w) 924(m) 916(m)	1595(m)	1040(m) 1022(m)	(22.2) 17.4, 16.2	15.75; $\epsilon$ , 76
<i>4</i> Cu <sub>2</sub> LCl <sub>4</sub> (H <sub>2</sub> O)·H <sub>2</sub> O	3420 <sup>e</sup> (m) 920(m) 911(m)	1598(m)	1045(m) 1023(m)	25.0 15.4	15.75; $\epsilon$ , 73
<i>5</i> Cu <sub>2</sub> LCl <sub>3</sub> (NO <sub>3</sub> )·H <sub>2</sub> O	3400 <sup>e</sup> (w)	1600(m)	1048(m) 1025(m)	25.0 (15.4)	15.70; $\epsilon$ , 66

<sup>a</sup>As nujol mull. <sup>b</sup>Shoulders are in parentheses. <sup>c</sup>In water. <sup>d</sup>Broad. <sup>e</sup>Very broad.

TABLE IV. Selected Distances (Å) and Angles (°).

Cu(1)–Cl(1)	2.170(4)	N(4)–C(10)	1.341(16)
Cu(1)–Cl(4)	2.168(6)	N(4)–C(14)	1.333(16)
Cu(1)–O(1)	2.386(9)	C(1)–C(2)	1.335(18)
Cu(1)–N(1)	2.049(10)	C(2)–C(3)	1.378(17)
Cu(1)–N(2)	2.027(9)	C(3)–C(4)	1.347(17)
Cu(2)–Cl(2)	2.641(4)	C(4)–C(5)	1.374(17)
Cu(2)–Cl(3)	2.200(4)	C(5)–C(6)	1.429(16)
Cu(2)–Cl(4)	2.130(6)	C(6)–C(7)	1.388(15)
Cu(2)–N(3)	2.039(10)	C(7)–C(8)	1.323(17)
Cu(2)–N(4)	2.002(12)	C(8)–C(9)	1.433(17)
N(1)–C(1)	1.325(15)	C(9)–C(10)	1.428(17)
N(1)–C(5)	1.341(14)	C(10)–C(11)	1.352(17)
N(2)–N(3)	1.286(12)	C(11)–C(12)	1.378(18)
N(2)–C(6)	1.348(15)	C(12)–C(13)	1.329(20)
N(3)–C(9)	1.301(14)	C(13)–C(14)	1.315(18)
Cl(1)–Cu(1)–Cl(4)	91.0(2)	Cu(2)–N(3)–C(9)	113.6(9)
Cl(1)–Cu(1)–O(1)	103.1(3)	N(2)–N(3)–C(9)	123.9(10)
Cl(1)–Cu(1)–N(1)	95.7(3)	Cu(2)–N(3)–N(2)	122.4(7)
Cl(1)–Cu(1)–N(2)	166.2(3)	Cu(2)–N(3)–C(9)	113.6(9)
Cl(4)–Cu(1)–O(1)	91.7(3)	N(2)–N(3)–C(9)	123.9(10)
Cl(4)–Cu(1)–N(1)	167.3(3)	N(1)–C(1)–C(2)	121.4(13)
Cl(4)–Cu(1)–N(2)	90.6(3)	C(1)–C(2)–C(3)	118.7(14)
O(1)–Cu(1)–N(1)	97.3(3)	C(2)–C(3)–C(4)	120.3(15)
O(1)–Cu(1)–N(2)	90.6(3)	C(3)–C(4)–C(5)	119.1(14)
N(1)–Cu(1)–N(2)	80.3(4)	N(1)–C(5)–C(4)	119.4(12)
Cl(2)–Cu(2)–Cl(3)	106.7(1)	N(1)–C(5)–C(6)	118.3(11)
Cl(2)–Cu(2)–Cl(4)	98.3(2)	C(4)–C(5)–C(6)	122.2(12)
Cl(2)–Cu(2)–N(3)	88.6(3)	N(2)–C(6)–C(5)	114.7(11)
Cl(2)–Cu(2)–N(4)	91.5(3)	N(2)–C(6)–C(7)	116.8(11)
Cl(3)–Cu(2)–Cl(4)	88.5(2)	C(5)–C(6)–C(7)	128.4(12)
Cl(3)–Cu(2)–N(3)	164.5(3)	C(6)–C(7)–C(8)	122.2(13)
Cl(3)–Cu(2)–N(4)	97.3(3)	C(7)–C(8)–C(9)	117.3(13)
Cl(4)–Cu(2)–N(3)	91.4(3)	N(3)–C(9)–C(8)	118.2(12)
Cl(4)–Cu(2)–N(4)	166.7(3)	N(3)–C(9)–C(10)	117.2(12)
N(3)–Cu(2)–N(4)	79.7(4)	C(8)–C(9)–C(10)	124.6(12)
Cu(1)–Cl(4)–Cu(2)	109.5(2)	N(4)–C(10)–C(9)	115.0(12)
Cu(1)–N(1)–C(1)	126.9(8)	N(4)–C(10)–C(11)	119.2(14)
Cu(1)–N(1)–C(5)	112.1(8)	C(9)–C(10)–C(11)	125.8(13)
C(1)–N(1)–C(5)	121.0(11)	C(10)–C(11)–C(12)	124.1(15)
Cu(1)–N(2)–N(3)	123.9(7)	C(11)–C(12)–C(13)	112.1(15)
Cu(1)–N(2)–C(6)	114.5(8)	C(12)–C(13)–C(14)	125.7(17)
N(3)–N(2)–C(6)	121.6(9)	N(4)–C(14)–C(13)	121.0(16)
Cu(2)–N(3)–N(2)	122.4(7)		

$[\text{Cu}_2\text{L}(\text{OH})(\text{H}_2\text{O})_3]^{3+}$ . The conditions of the different reaction and crystallization procedures thus influence a series of equilibria concerned with ligand metathesis and with solubility of the final products. This view is also supported by the coincidence of the absorption maxima in the electronic spectra of complexes 3–5 in aqueous solution (Table III).

Complex 4 has a solid state structure (see below) in which both copper atoms achieve a square-pyramidal coordination, due to the presence of a ligating water molecule which is also detectable

in the I.R. spectrum which shows the characteristic bands at 920 and 911  $\text{cm}^{-1}$ . The structural features of complex 5 are not obvious. While the reflectance spectra of 5 and 4 are very similar showing maxima at 25.0 and 15.4 kK, no water molecules are shown by the I.R. spectrum within the coordination spheres of neither copper atoms. Thus the observed general tendency to pentacoordination might be satisfied either by a structure in which the nitrate ligand is somehow bridging the metal centres, or by a polymeric arrangement in which terminal chlorine atoms are bridging copper atoms of different molecular

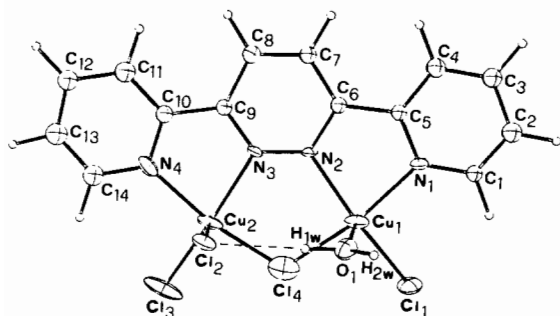


Fig. 1.

units. Unfortunately, X-ray structural determinations of compound 5 were impossible due to the difficulty in growing suitable crystals.

#### Description of the Structure of 4

The crystal structure of 4 consists of dinuclear  $[\text{Cu}_2\text{LCl}_4(\text{H}_2\text{O})]$  complexes and of interposed water molecules. The two copper atoms are penta-coordinated in a square-pyramidal arrangement (Fig. 1).

Bond distances and angles in the complex are given in Table IV.

For each copper atom the basal coordinated atoms are two chlorine atoms – one of which is bridging the metals – and two chelating nitrogen atoms of the organic ligand. The apical ligands – the coordinated water molecule and a chlorine atom – lie on the same side with respect to the basal plane; they are involved in an intramolecular hydrogen bond, the  $\text{Cl}(2)\cdots\text{H}(1)\text{w}$  distance being 2.28 Å. The copper atoms Cu(1) and Cu(2) are displaced from the mean basal planes by 0.214 and 0.241 Å, respectively, in the direction of the apical ligands.

A comparison of distances and angles in the title complex with those of the otherwise similar  $\mu$ -hydroxo complex 3 reveals no significant differences

for the Cu–Cl, Cu–N and Cu–O<sub>w</sub> bonds. However the longer Cu–Cl<sub>μ</sub> distances with respect to the Cu–O<sub>μ</sub> distances allow the Cu $\cdots$ Cu separation in the present complex to assume a value (3.51 Å) larger than that found both in complex 3 (3.38 Å) and in the polymeric complex  $[\text{Cu}_2\text{LCl}_2(\text{OH})(\text{H}_2\text{O})]_n\text{Cl}_n \cdot 2n\text{H}_2\text{O}$  (3.39 Å) [8]. The Cu $\cdots$ Cu separation, therefore, seems to be influenced much more by the bridging atom than by the organic ligand which, on the contrary, shows a fair tendency to adapt itself to the structural demand of the inorganic moiety. This observation becomes more evident when considering the relevant deviations from the ideal  $sp^2$  geometry undergone by C<sub>5</sub>, C<sub>6</sub>, C<sub>9</sub> and C<sub>10</sub> carbon atoms as soon as the intermetallic distance shortens with respect to the 'ideal' value of 4.15 Å which would leave the ligand undistorted.

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