

## Crystal Structure Determination of Dichlorobis[1-(2-Pyridylmethyl)imidazole]-Copper(II). A Polymeric Copper Complex

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The crystal structure of the title compound has been determined from three dimensional X-ray data. The crystal belongs to the space group  $P\bar{1}$  with  $Z = 2$  (for a monomeric unit) with unit cell dimensions  $a = 7.75(2)$ ,  $b = 9.81(2)$ ,  $c = 14.63(1)$  Å,  $\alpha = 74.50(5)$ ,  $\beta = 80.15(5)$ ,  $\gamma = 87.77(5)^\circ$ . The structure was solved by the heavy-atom method and refined by least-squares techniques to  $R$  10.4 for 1656 observed reflections. The copper is in a roughly trigonal bipyramidal environment. The crystal structure consists of polymeric chains of copper centers linked by attachment of the pyridyl group to the adjacent copper ion.

### Introduction

A detailed study of the coordination behavior of several 1-(2-pyridyl)imidazoles and 1-(2-pyridylmethyl)imidazoles with first-row transition metals has been undertaken [1]. This work was intended to determine whether a potential bidentate coordination mode of the ligands involving carbon–metal bonding [2] (imidazole C-2 and pyridine N) would compete with the normal imidazole (N-3) coordination in such ligands [3]. Solution NMR studies have indicated that imidazole is predominantly bound *via* N-3 to first row metal ions ( $\text{Co}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Fe}^{\text{II}}$ ) and in two solid cobalt salts the pyridine-N remained uncoordinated [1]. In the present work the structure of a hydrate of dichlorobis[1-(2-pyridylmethyl)imidazole]copper(II) was determined, in order to establish the structural situation in a solid copper salt.

### Experimental

The complex was prepared by mixing a 2:1 molar ratio of 1-(2-pyridylmethyl)imidazole with  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in methanol and allowing the solution to slowly evaporate. The blue crystals were of poor quality. Many crystals were examined and the 'best' crystal was used in the crystal structure determination.

Crystal data:  $\text{Cu}(\text{C}_9\text{H}_9\text{N}_2)_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ ,  $M = 471$ ,  $a = 7.75(2)$ ,  $b = 9.81(2)$ ,  $c = 14.63(1)$  Å,  $\alpha = 74.50(5)$ ,  $\beta = 80.15(5)$ ,  $\gamma = 87.77(5)^\circ$ ,  $D_c = 1.49$ ,  $D_o = 1.45$   $\text{gcm}^{-3}$ ,  $Z = 2$  (monomeric unit,  $F(000) = 482$ , space group  $P\bar{1}$ ,  $U = 1057$  Å<sup>3</sup>,  $\mu\text{MoK}\alpha = 13.5$   $\text{cm}^{-1}$ ).

### Intensity Measurements

Preliminary cell dimensions were obtained using the Enraf-Nonius program SEARCH to locate 15 independent reflections. Refined cell dimensions and their estimated standard deviations were calculated from a least-squares refinement of the preliminary values against the observed values of  $\pm\theta$  for 23 strong general reflections.

Diffraction data were collected from a small crystal mounted on a glass fiber with epoxy resin. The diffraction pattern for the complex was examined by the omega-scan technique and a second smaller peak was observed in several reflections. While these reflections represented a small proportion of the whole, crystal splitting was indicated. When all efforts to obtain a better crystal were unsuccessful, work on this crystal was continued with this problem in mind (*vide infra*).

The diffraction intensities were measured at 293 °K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP8/E computer, using  $\text{MoK}\alpha$  radiation from a highly oriented graphite monochromator. The  $\theta$ – $2\theta$  scan technique was used to record the intensities of all reflections for which  $1^\circ < \theta < 44^\circ$ . The symmetric scans were centered on the calculated peak positions ( $\lambda(\text{MoK}\alpha)$ , 0.7107 Å). Scan widths (sw) were based on  $\theta$  using the formula  $\text{sw} = A + B \tan\theta$  where  $A = 1.2$  and  $B = 0.3$ . For each reflection, the calculated scan angle was extended by 25% at either side to estimate the background count. Reflection data were considered significant if intensities registered 10 counts above background during a rapid prescan, while insignificant reflections were automatically rejected by the computer. 2101 independent intensities were recorded, of which 1785 had  $F^2 > 3\sigma(F_o^2)$ , where  $F_o^2$  was estimated from the counting statistics. During the data collection, the

TABLE I. Positional and Thermal Parameters and Their Estimated Standard Deviations for  $\text{Cu}(\text{C}_9\text{H}_9\text{N}_2)_2\text{Cl}_2 \cdot \text{H}_2\text{O}^a$ 

Atom	X	Y	Z	B(1.1)	B(2.2)	B(3.3)	B(1.2)	B(1.3)	B(2.3)
Cu	0.1506(3)	-0.0340(2)	0.2723(2)	0.0095(3)	0.0092(2)	0.0032(1)	0.0006(5)	-0.0050(3)	-0.0007(3)
Cl1	0.0895(7)	0.1659(5)	0.3325(3)	0.0208(10)	0.0084(5)	0.0059(3)	0.005(1)	-0.0087(8)	-0.0051(6)
Cl2	0.3435(6)	-0.0846(6)	0.1439(3)	0.0115(9)	0.0195(7)	0.0029(2)	-0.001(1)	-0.0084(7)	-0.0044(7)
O	0.548(3)	0.661(2)	0.698(1)	9.9(6)					
N1	1.005(2)	-0.243(1)	0.3494(9)	2.7(3)					
N8	0.569(2)	-0.132(1)	0.4200(10)	3.1(3)					
N10	0.323(2)	-0.096(1)	0.3597(9)	2.6(3)					
N1'	-0.340(2)	0.447(2)	0.1135(12)	5.2(4)					
N8'	-0.247(2)	0.121(1)	0.1141(9)	2.8(3)					
N10'	-0.035(2)	0.016(1)	0.1920(9)	2.4(3)					
C2	0.839(2)	-0.262(2)	0.392(1)	2.9(4)					
C3	0.760(3)	-0.390(2)	0.409(2)	6.1(6)					
C4	0.854(4)	-0.500(3)	0.383(2)	7.9(7)					
C5	1.024(3)	-0.481(2)	0.337(2)	6.4(6)					
C6	1.101(3)	-0.350(2)	0.320(1)	4.8(5)					
C7	0.757(2)	-0.141(2)	0.420(1)	2.9(4)					
C9	0.495(2)	-0.094(2)	0.337(1)	2.8(4)					
C11	0.281(2)	-0.136(2)	0.458(1)	3.3(4)					
C12	0.433(2)	-0.159(2)	0.497(1)	3.3(4)					
C2'	-0.317(2)	0.375(2)	0.050(1)	3.5(4)					
C3'	-0.243(3)	0.435(2)	-0.046(2)	5.3(5)					
C4'	-0.191(3)	0.576(2)	-0.071(2)	5.5(5)					
C5'	-0.213(3)	0.651(2)	-0.016(2)	5.5(5)					
C6'	-0.288(3)	0.585(2)	0.085(2)	6.3(6)					
C7'	-0.387(3)	0.223(2)	0.086(1)	4.5(5)					
C9'	-0.139(3)	0.128(2)	0.179(1)	4.0(4)					
C11'	-0.082(3)	-0.064(2)	0.136(1)	4.0(4)					
C12'	-0.213(2)	0.000(2)	0.091(1)	2.7(4)					
H3	0.634(3)	-0.404(2)	0.440(2)	5.0					
H4	0.797(4)	-0.595(3)	0.401(2)	5.0					
H5	1.085(3)	-0.560(2)	0.314(2)	5.0					
H6	1.227(3)	-0.338(2)	0.288(1)	5.0					
H71	0.815(2)	-0.054(2)	0.373(1)	5.0					
H72	0.780(2)	-0.145(2)	0.486(1)	5.0					
H9	0.565(2)	-0.068(2)	0.269(1)	5.0					
H11	0.158(2)	-0.148(2)	0.497(1)	5.0					
H12	0.441(2)	-0.189(2)	0.568(1)	5.0					
H3'	-0.227(3)	0.379(2)	-0.095(2)	5.0					
H4'	-0.134(3)	0.617(2)	-0.139(2)	5.0					

H5'	-0.179(3)	0.754(2)	-0.040(2)	5.0
H6'	-0.299(3)	0.646(2)	0.132(2)	5.0
H71'	-0.440(3)	0.198(2)	0.034(1)	5.0
H72'	-0.482(3)	0.217(2)	0.143(1)	5.0
H9'	-0.139(3)	0.208(2)	0.212(1)	5.0
H11'	-0.025(3)	-0.157(2)	0.130(1)	5.0
H12'	-0.273(2)	-0.039(2)	0.047(1)	5.0

<sup>a</sup>The form of the anisotropic thermal parameter is:  $\exp[-(B(1.1)*H*H + B(2.2)*K*K + B(3.3)*L*L + B(1.2)*H*K + B(1.3)*H*L + B(2.3)*K*L)]$ .

intensities of four standard reflections were monitored at 100 reflection intervals and showed no greater fluctuations than those expected from Poisson statistics. The raw intensity data was corrected for Lorentz and polarization effects, but not for absorption.

Full-matrix least-squares refinement was based on  $F$ , and the function minimized as  $\sum w(|F_o| - |F_c|)^2$ . The atomic scattering factors were taken from Cromer and Waber [4] and those for hydrogen from Stewart *et al.* [5]. The effects of anomalous dispersion were included in  $F_c$  using Cromer's [6] values for  $\Delta f'$  and  $\Delta f''$ . Agreement factors are defined as  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $R_w = \sum (|F_o| - |F_c|)^2 / \sum w |F_o|^2$ .

#### Solutions and Refinement of the Structure

Patterson functions located the Cu and the two chlorine atoms. The remaining non-hydrogen atoms were located from Fourier difference maps ( $R = 16.1\%$ ).

The reflection data had clearly been affected by the crystal splitting mentioned previously. In an attempt to improve the data, 129 of the worst affected reflections were removed from the calculation, whereupon the model converged with  $R = 12.5\%$  for the 1656 reflections. Hydrogen atoms were inserted as fixed atoms at their calculated positions with fixed temperature factors  $\beta = 5.0$ , assuming C-H = 1.0 Å. During refinement anisotropic temperature factors were introduced only for the copper and chlorine atoms. The model converged with  $R = 10.4\%$  and  $R_w = 12.7\%$ .

The error in an observation of unit weight is 4.8. A final structure factor calculation with all observed and unobserved reflections included (no refinement) gave  $R = 14.5\%$ . The high value of the  $R$  for the crystal is attributed to the crystal splitting mentioned above; on this basis it was decided that careful measurement of reflections rejected automatically during the data collection would not significantly improve the results. A final Fourier difference map was produced and was featureless. The final positional and thermal parameters are listed in Table I. A table of calculated and observed structure factor amplitudes is available from the editor on request.

#### Results and Discussions

As discussed previously, the crystals of  $\text{Cu}(\text{C}_9\text{H}_9\text{N}_3)_2\text{Cl}_2 \cdot \text{H}_2\text{O}$  were of rather low equality and this limits the accuracy of the final data. The coordination environment of the metal atom and other bond connectivities are clearly evident however. The copper atom has a trigonal bipyramidal ligand environment with distortion towards square pyramidal geometry. The bond lengths and angle data

TABLE II. Bond Lengths for  $\text{Cu}(\text{C}_9\text{H}_9\text{N}_3)_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ .

$\text{Cu}-\text{N}(1)^a$	2.290(6)	$\text{C}(4)-\text{C}(5)$	1.37(1)
$\text{Cu}-\text{N}(10)$	1.976(6)	$\text{C}(5)-\text{C}(6)$	1.38(1)
$\text{Cu}-\text{N}(10')$	1.976(6)	$\text{C}(9)-\text{N}(10)$	1.32(1)
$\text{N}(1)-\text{C}(2)$	1.33(1)	$\text{C}(11)-\text{C}(12)$	1.39(1)
$\text{N}(1)-\text{C}(6)$	1.39(1)	$\text{C}(12)-\text{N}(8)$	1.38(1)
$\text{N}(8)-\text{C}(7)$	1.46(1)	$\text{N}(1')-\text{C}(2')$	1.29(1)
$\text{N}(8)-\text{C}(9)$	1.39(1)	$\text{N}(1')-\text{C}(6')$	1.36(1)
$\text{N}(8)-\text{C}(12)$	1.38(1)	$\text{N}(8')-\text{C}(7')$	1.48(1)
$\text{N}(10)-\text{C}(11)$	1.37(1)	$\text{N}(8')-\text{C}(9')$	1.39(1)
$\text{C}(2)-\text{C}(3)$	1.36(1)	$\text{N}(8')-\text{C}(12')$	1.33(1)
$\text{C}(2)-\text{C}(7)$	1.44(1)	$\text{N}(10')-\text{C}(9')$	1.33(1)
$\text{C}(3)-\text{C}(4)$	1.37(1)	$\text{N}(10')-\text{C}(11')$	1.37(1)
$\text{Cu}-\text{Cl}(1)$	2.356(2)	$\text{C}(2')-\text{C}(3')$	1.40(1)
$\text{Cu}-\text{Cl}(2)$	2.344(2)	$\text{C}(2')-\text{C}(7')$	1.53(1)
		$\text{C}(3')-\text{C}(4')$	1.39(1)
		$\text{C}(4')-\text{C}(5')$	1.21(1)
		$\text{C}(11')-\text{C}(12')$	1.35(1)
		$\text{C}(5')-\text{C}(6')$	1.48(1)

<sup>a</sup>Intermolecular.

are given in Tables II and III. The ligand numbering system adopted is given in Figure 1. The coordination geometry is usefully discussed in terms of the planes defined in Table IV. The equatorial plane I is nearly orthogonal to the apical ligand planes (II, III, IV). The  $\text{N}10-\text{Cu}-\text{N}10'$  bond angle is  $175^\circ$ . The angles between the apical planes are  $59^\circ$ ,  $47^\circ$  and  $76^\circ$  compared to the  $60^\circ$  required for undistorted trigonal bipyramidal geometry. The pyridine and imidazole

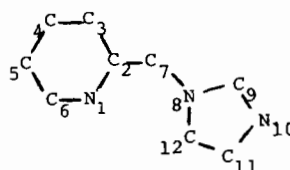


Figure 1. Numbering scheme for ligand molecules.

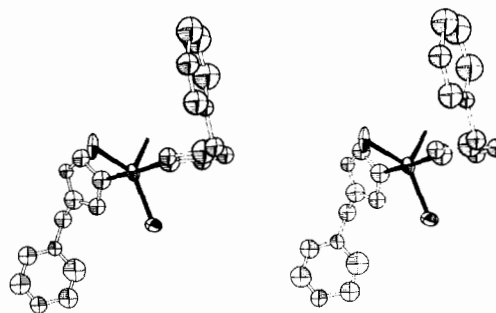


Figure 2. Coordination geometry at copper.

rings in the ligand molecule which is involved in polymeric bridging are at right angles to one another, while the corresponding interplanar angle is  $71^\circ$  in the non-bridging ligand molecule. The pyridine and imidazole ring planes are close to planarity. The involvement of the pyridine rings in metal coordination contrasts to the results in analogous

TABLE III. Bond Angles for  $\text{Cu}(\text{C}_9\text{H}_9\text{N}_3)_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ .

$\text{N}(1)-\text{Cu}-\text{N}(10)$	87.2(2)	$\text{N}(1)-\text{C}(6)-\text{C}(5)$	119(1)
$\text{N}(1)-\text{Cu}-\text{N}(10')$	88.5(2)	$\text{N}(8)-\text{C}(7)-\text{C}(2)$	114.4(7)
$\text{N}(1)-\text{Cu}-\text{Cl}(1)$	119.9(2)	$\text{N}(8)-\text{C}(9)-\text{N}(10)$	109.7(7)
$\text{N}(1)-\text{Cu}-\text{Cl}(2)$	104.6(2)	$\text{N}(10)-\text{C}(11)-\text{C}(12)$	109.0(8)
$\text{N}(10)-\text{Cu}-\text{N}(10')$	175.5(3)	$\text{C}(11)-\text{C}(12)-\text{N}(8)$	105.8(8)
$\text{N}(10)-\text{Cu}-\text{Cl}(1)$	89.4(2)	$\text{C}(2')-\text{N}(1')-\text{C}(6')$	118.3(9)
$\text{N}(10)-\text{Cu}-\text{Cl}(2)$	91.6(2)	$\text{C}(7')-\text{N}(8')-\text{C}(9')$	125.6(7)
$\text{N}(10')-\text{Cu}-\text{Cl}(1)$	91.6(2)	$\text{C}(7')-\text{N}(8')-\text{C}(12')$	127.2(7)
$\text{N}(10')-\text{Cu}-\text{Cl}(2)$	90.7(2)	$\text{C}(9')-\text{N}(8')-\text{C}(12')$	106.9(7)
$\text{Cl}(1)-\text{Cu}-\text{Cl}(2)$	135.5(1)	$\text{Cu}-\text{N}(10')-\text{C}(9')$	129.8(6)
$\text{Cu}-\text{N}(1)-\text{C}(2)$	128.5(5)	$\text{Cu}-\text{N}(10')-\text{C}(11')$	124.8(6)
$\text{Cu}-\text{N}(1)-\text{C}(6)$	107.8(6)	$\text{C}(9')-\text{N}(10')-\text{C}(11')$	105.4(7)
$\text{C}(2)-\text{N}(1)-\text{C}(6)$	121.3(7)	$\text{N}(1')-\text{C}(2')-\text{C}(3')$	122.4(9)
$\text{C}(7)-\text{N}(8)-\text{C}(9)$	123.5(7)	$\text{N}(1')-\text{C}(2')-\text{C}(7')$	115.4(8)
$\text{C}(7)-\text{N}(8)-\text{C}(12)$	129.0(7)	$\text{C}(3')-\text{C}(2')-\text{C}(7')$	122.1(9)
$\text{C}(9)-\text{N}(8)-\text{C}(12)$	107.5(7)	$\text{C}(2')-\text{C}(3')-\text{C}(4')$	117(1)
$\text{Cu}-\text{N}(10)-\text{C}(9)$	127.8(6)	$\text{C}(3')-\text{C}(4')-\text{C}(5')$	125(1)
$\text{Cu}-\text{N}(10)-\text{C}(11)$	123.9(6)	$\text{C}(4')-\text{C}(5')-\text{C}(6')$	117(1)
$\text{C}(9)-\text{N}(10)-\text{C}(11)$	108.1(7)	$\text{C}(5')-\text{C}(6')-\text{N}(1')$	120(1)
$\text{N}(1)-\text{C}(2)-\text{C}(3)$	120.0(9)	$\text{N}(8')-\text{C}(7')-\text{C}(2')$	111.5(7)
$\text{N}(1)-\text{C}(2)-\text{C}(7)$	114.8(7)	$\text{N}(8')-\text{C}(9')-\text{N}(10')$	109.9(8)
$\text{C}(3)-\text{C}(2)-\text{C}(7)$	125.2(9)	$\text{N}(10')-\text{C}(11')-\text{C}(12')$	109.9(8)
$\text{C}(2)-\text{C}(3)-\text{C}(4)$	120(1)	$\text{N}(8')-\text{C}(12')-\text{C}(11')$	107.8(7)
$\text{C}(3)-\text{C}(4)-\text{C}(5)$	121(1)		
$\text{C}(4)-\text{C}(5)-\text{C}(6)$	119(1)		

TABLE IV. Coefficients for Least-Squares Planes for the Equation  $AX + BY + CZ - D$  for  $\text{Cu}(\text{C}_9\text{H}_9\text{N}_2)_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ .

Plane														
I	N(1) Cl(1) Cl(2)	-.7997	.1351	-.5850	-3.5928	N(1), 0; Cl(1), 0; Cl(2), 0; Cu, .0086; N(10), -2.0636; N(10'), 1.9491								
II	N(10) N(10') N(1)	.3911	-.6334	-.667	-2.2274	N(10), 0; N(10'), 0; N(1), 0; Cu, -.0269;								
III	N(10) N(10') Cl(1)	.5630	.3273	-.7436	-1.5223	N(10), 0; N(10'), 0; Cl(1), 0; Cu, .0179; Cl(2), 1.6929; N(1), 2.6221								
IV	N(10) N(10') Cl(2)	.3243	.9065	-.2702	.1778	N(10), 0; N(10'), 0; Cl(2), 0; Cu, .0430; Cl(1), 1.7411; N(1), .3660								
V	N(1) C(2) C(3) C(4) C(5) C(6)	-.4571	.0325	-.8888	-8.2311	N(1), .0050; C(2), -.0035; C(3), -.0154; C(4), .0348; C(5), -.0333; C(6), .0124								
VI	N(8) C(9) N(10) C(11) C(12)	-.0641	-.9979	-.0127	-.7160	N(8), .0049; C(9), -.0040; N(10), .0011; C(11), .0025; C(12), -.0046; Cu, -.1601								
VII	N(1') C(2') C(3') C(4') C(5') C(6')	-.9564	.1961	-.2165	2.6853	N(1'), .0450; C(2'), -.0740; C(3'), .0643; C(4'), -.0253; C(5'), -.0015; C(6'), -.0085								
VIII	N(8') N(10') C(9') C(11') C(12')	.5719	.2649	-.7764	-1.7026	N(8'), .0184; N(10'), .0350; C(9'), -.0329; C(11'), -.0262; C(12'), .0057								
<i>Interplanar Angles (°)</i>														
I, II	I, III	I, IV	I, V	I, VI	I, VIII	II, III	II, IV	II, V	II, VI	II, VIII	III, IV	III, V	III, VI	I II, VIII
89.6	89.3	88.8	27.2	85.6	88.1	59.9	74.5	66.8	52.0	55.0	46.6	66.1	69.2	4.1
IV, V	IV, VI	IV, VIII	V, VI	V, VIII	VI, VIII	VII, VIII								
83.0	22.8	50.6	89.5	64.1	73.1	70.9								

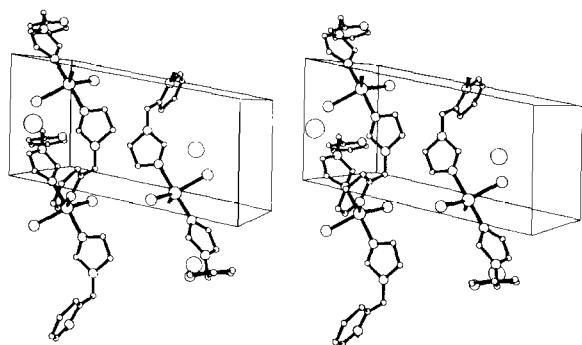


Figure 3. Unit cell and portion of polymeric chain.

cobalt complexes where the pyridine is uncoordinated and the cobalt is tetrahedrally coordinated [1].

The bond lengths for Cu-N and Cu-Cl bonds in this structure are similar to those found in  $\text{Cu}(\text{imidazole})_2\text{Cl}_2$  [7]. The apical position in  $\text{Cu}(\text{Im})_2\text{Cl}_2$  is occupied by a chloride ion from an adjacent Cu center and the structure of  $\text{Cu}(\text{Im})_2\text{Cl}_2$  is essentially a tetragonal pyramid.

Because of the internuclear bridging of the one pyridyl group the complex exists as infinite polymeric chains of five-coordinate copper atoms, coordinated to two halogens, two imidazole nitrogens (N10) and to the pyridine nitrogen (N1) of the next mole-

cule in the  $a$  direction. The five-coordinate geometry of the asymmetric unit is shown as a stereoscopic pair view in Figure 2, and Figure 3 shows the molecular packing and two links of the infinite chain.

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