

## Crystal Structure of [2,6-Bis(3,5-dimethyl-*N*-pyrazolyl)pyridine]-(azido)(chloro)copper(II)

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In the title compound, the coordination around the Cu atom is a distorted square-pyramid involving three N atoms from the ligand and one N atom from the azido group at the basal plane. The Cl atom is located at the apical position. The Cu atom is 0.32(5)Å above the basal plane. There are three intramolecular and four weak intermolecular hydrogen bonds in the structure. IR spectra confirm the asymmetric N<sub>3</sub> stretching vibrations of the terminal azide group.

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The chemical and spectroscopic properties of mononuclear copper complexes of pyrazole and its derivatives have been of great interest in recent years.<sup>1-3</sup> This is mainly because of manipulation in making model compounds like tyrosinase and hemocyanin for biological systems.<sup>4</sup>

A solution of 2,6-bis(3,5-dimethyl-*N*-pyrazolyl)<sup>5</sup> (0.266 g, 1 mmol) in hot acetonitrile (20 ml) was added to CuCl<sub>2</sub>·2H<sub>2</sub>O (0.171 g, 1 mmol) in hot MeOH (20 ml). A solution of NaN<sub>3</sub> (0.65 g, 1 mmol) in water (5 ml) was added to this mixture. The resulting mixture was set aside for three days and the dark-green crystals which formed were filtered off and dried in air. The synthesis and chemical structure of the title compound is shown in Fig. 1. The IR spectrum of the [2,6-bis(3,5-dimethyl-*N*-pyrazolyl)pyridine](azido)(chloro)copper(II) shows the characteristic asymmetric N<sub>3</sub> stretching vibrations of the terminal azide group at 2067 cm<sup>-1</sup>. The IR spectra were recorded on a Mattson 1000 FTIR.

In this study of [Cu(C<sub>15</sub>H<sub>17</sub>N<sub>5</sub>)(N<sub>3</sub>)Cl], the structure consists of asymmetric monomers which have a triclinic unit cell containing two molecules. The complex possesses the first coordination sphere including both halide (Cl) and pseudohalide (N<sub>3</sub>) ligands. A mononuclear copper complex with a similar coordination sphere was previously investigated.<sup>6</sup>

As can be seen in Fig. 2, and the copper atom has a distorted-square pyramidal geometry the five nearest neighbours around the Cu atom are the three N atoms [Cu-N1 2.057(3), Cu-N3

1.982(3), Cu-N5 2.051(3)Å] from the 2,6-bis(3,5-dimethyl-*N*-pyrazolyl) ligand and an N atom [Cu-N6 1.928(3)Å] from the azido group occupying the basal plane. The axial position is occupied by the Cl atom [Cu-Cl 2.4677(12)Å]. The copper atom is located 0.32(5)Å above the plane formed by N1/N3/N5/N6. A significant deviation of the basal plane is also evident from angles N1-Cu-N5 and N3-Cu-N6 with values of 152.76(13) and 158.45(16)°, respectively. The azido group is almost linear with an N6-N7-N8 bond angle of 177.0(5)°.

The crystal and experimental data are given in Table 1 and the final atomic parameters are presented in Table 2. Some of the important coordinative bonds and angles are given in Table 3. The possible hydrogen bonds indicate three intermolecular hydrogen bonds. These hydrogen bonds are rather weak interactions, as can be seen from the details given in Table 4.

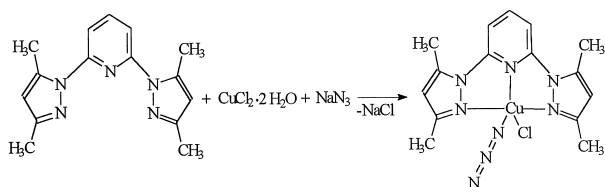


Fig. 1 Synthesis and chemical structure.

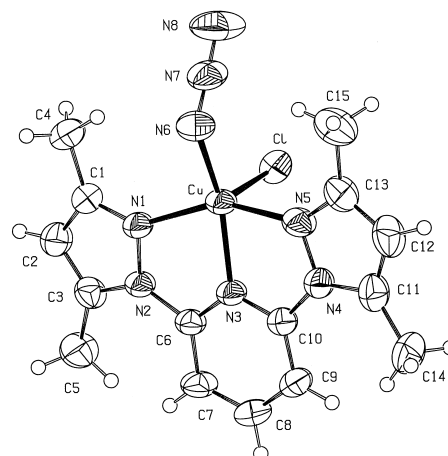


Fig. 2 Molecular structure of the title compound, showing 50% probability displacement ellipsoids.

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Table 1 Crystal and experimental data

Formula: C <sub>15</sub> H <sub>17</sub> N <sub>8</sub> ClCu
Formula weight = 408.35
Space group: <i>P</i> $\bar{1}$
Crystal system: triclinic
<i>a</i> = 8.6450(12) Å
<i>b</i> = 10.0026(11) Å
<i>c</i> = 10.7953(13) Å
$\alpha$ = 111.297(3)°
$\beta$ = 96.260(2)°
$\gamma$ = 93.958(4)°
<i>V</i> = 858.59(18) Å <sup>3</sup>
<i>D<sub>x</sub></i> = 1.580 g/cm <sup>3</sup>
$\mu$ (Cu K $\alpha$ ) = 3.367 mm <sup>-1</sup>
<i>T</i> = 293 K
Color = dark green
Radiation Cu K $\alpha$ ( $\lambda$ = 1.5418 Å)
0.30 × 0.25 × 0.20 mm
2 $\theta$ <sub>max</sub> = 74.2°
No. of reflections = 3463
No. of reflection used = 3149 ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))
No. of parameters = 227
<i>R</i> = 0.067
<i>R<sub>w</sub></i> = 0.185
Goodness-of-fit = 1.12
( $\Delta\rho$ ) <sub>max</sub> = 0.73 eÅ <sup>-3</sup>
( $\Delta\rho$ ) <sub>min</sub> = -0.61 eÅ <sup>-3</sup>
Measurement: Enraf-Nonius CAD-4
Program system: WinGX package
Structure determination: SHELXS97
Refinement: full matrix least-square SHELXL97
Treatment of hydrogen atoms: geometric calculation

## Acknowledgements

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## References

1. P. Manikandan, K. R. J. Thomas, and P. T. Manoharan, *Acta Crystallogr.*, **2000**, C52, 308.
2. P. Manikandan, K. R. J. Thomas, and P. T. Manoharan, *J. Chem. Soc., Dalton Trans.*, **2000**, 2779.
3. N. Kitajima, K. Fujisawa, C. Fujimoto, Y. Moro-oka, S. Hashimoto, T. Kitagawa, K. Toriumi, K. Tatsumi, and A. Nakamura, *J. Am. Chem. Soc.*, **1992**, 114, 1277.
4. E. I. Solomon, M. J. Baldwin, and M. D. Lowery, *Chem. Rev.*, **1992**, 92, 521.
5. D. L. Jameson and K. A. Goldsby, *J. Org. Chem.*, **1990**, 55, 4992.

Table 2 Final atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B<sub>eq</sub></i>
Cu	0.65960(6)	0.90632(5)	0.68914(4)	3.57(2)
Cl	0.86112(11)	0.73925(11)	0.66746(10)	4.55(3)
N1	0.4978(4)	0.7691(3)	0.5327(3)	3.51(6)
N2	0.5302(4)	0.7696(3)	0.4101(3)	3.40(6)
N3	0.7059(3)	0.9645(3)	0.5388(3)	3.24(6)
N4	0.8655(4)	1.1513(3)	0.6991(3)	3.80(7)
N5	0.8058(4)	1.0952(3)	0.7858(3)	4.10(7)
N6	0.5581(5)	0.9000(5)	0.8376(3)	5.27(10)
N7	0.5968(5)	0.8285(5)	0.9006(3)	5.47(11)
N8	0.6296(8)	0.7628(6)	0.9648(5)	8.16(16)
C1	0.3929(4)	0.6550(4)	0.5035(4)	3.85(8)
C2	0.3577(5)	0.5826(4)	0.3646(4)	4.22(9)
C3	0.4448(5)	0.6552(4)	0.3069(4)	3.83(8)
C4	0.3252(5)	0.6175(5)	0.6091(5)	4.75(10)
C5	0.4546(6)	0.6191(5)	0.1610(4)	5.29(11)
C6	0.6404(4)	0.8820(4)	0.4144(3)	3.27(7)
C7	0.6813(5)	0.9085(4)	0.3038(4)	4.11(9)
C8	0.7957(5)	1.0203(5)	0.3289(4)	4.35(9)
C9	0.8643(5)	1.1080(4)	0.4577(4)	4.04(8)
C10	0.8130(4)	1.0757(4)	0.5613(3)	3.47(7)
C11	0.9716(5)	1.2706(4)	0.7684(5)	4.63(10)
C12	0.9804(6)	1.2876(5)	0.9006(5)	5.47(12)
C13	0.8754(6)	1.1773(5)	0.9078(4)	5.01(11)
C14	1.0564(6)	1.3625(5)	0.7088(6)	5.66(13)
C15	0.8412(8)	1.1497(8)	1.0286(5)	7.33(15)

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i \cdot a_j)$$

Table 3 Selected bond distances (Å) and angles (°)

Cu-Cl	2.4677(12)	Cu-N5	2.051(3)
Cu-N1	2.057(3)	Cu-N6	1.928(3)
Cu-N3	1.982(3)		
N6 N7 N8	177.0(5)	N1 Cu Cl	96.80(9)
N6 Cu N3	158.45(16)	N6 Cu N5	99.24(15)
N3 Cu N5	77.49(12)	N6 Cu N1	99.25(15)
N3 Cu N1	77.95(11)	N5 Cu N1	152.76(13)
N6 Cu Cl	105.25(13)	N3 Cu Cl	96.30(9)
N5 Cu Cl	97.42(10)		

Table 4 Hydrogen bonding geometry (Å, °)

D-H...A	D-H	H...A	D-A	D-H...A
C2 H2 Cl <sup>i</sup>	0.9300	2.6900	3.5028	146.42
C7 H7 N8 <sup>ii</sup>	0.9300	2.5337	3.3760	150.78
C9 H9 Cl <sup>iii</sup>	0.9300	2.6567	3.3903	136.28

Symmetry codes: (i) 1-x, 1-y, 1-z (ii) x, y, 1+z (iii) -x, -y, 1-z.

6. R. Cortes, L. Lezama, J. I. R. Larramendi, M. Insausti, J. V. Folgado, G. Madariga, and T. Rojo, *J. Chem. Soc., Dalton Trans.*, **1994**, 2573.