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Crystal Structure of Dichloro(1-phenylpyrazole-N^2)copper(II)

by M. Małecka[1], T.A. Olszak[1], A. Rybarczyk-Pirek[1] and K. Kostka[2]

[1]*Department of Crystallography, University of Łódź, Pomorska 149/153, 90-236 Łódź, Poland*
[2]*Institute of Chemistry, Faculty of Pharmacy, Medical University, Muszyńskiego 1, 90-151 Łódź, Poland*

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The crystal structure of dichloro(1-phenylpyrazole-N^2)copper(II) has been determined from X-ray diffraction data collected on single-crystal mounted in capillary at room temperature. Crystal data: $CuCl_2(C_9H_8N_2)$, triclinic system, P-1, $a = 8.534(2)$, $b = 10.047(2)$, $c = 6.311(2)$ Å, $\alpha = 105.21(3)$, $\beta = 93.45(3)$, $\gamma = 81.72(2)°$, $Z = 2$. The structure was solved by directed methods and refined to $R = 0.047$ for 1089 observed reflections. The geometry around the Cu^{2+} ion is best described as square-pyramidal (SQP). The molecules form chains.

The title compound (1) was obtained by M. Strawiak [1] by mixing hot ethanolic solution of $CuCl_2H_2O$ and 1-phenylpyrazole in molar ratio 1:1 (Scheme 1). Single crystals began to separate at room temperature. The complex was filtered and washed three times with cold solvent and dried in vacuum above phosphorus pentaoxide. A brown crystal of size 0.4×0.3×0.3 mm was used for measurements on AFC5S Rigaku diffractometer. Crystal mounted in glass capillary. Cell parameters were obtained from least-squares treatment of 25 reflections in θ range 26.65–44.47°. Intensities were collected using graphite monochromatized CuK_α radiation and ω scan. Three standard reflections: 0 1 -3, 1 -1 -1, 0 -2 -3, checked every 150 measurements, showed no significant change of intensity during data collection. 1325 independent reflections measured in the range h: $0\rightarrow-6$, k: $-11\rightarrow11$, l: $-7\rightarrow7$, of which 1089 were observed with $I > 2\sigma(I)$. Intensities were corrected for Lorentz and polarization effect [2] and also absorption effect [3]. The structure was solved by direct methods using SHELXS86 [4] program and refined by full-matrix least squares calculation on F^2 using SHELXL97 [5]. After the refinement with isotropic temperature factors, the refinement was continued with anisotropic temperature factors for non-H atoms. Positions of H-atoms were found on Fourier difference map and refined using the riding model. Empirical isotropic extinction parameter x was used to correct F_c according $F_c^* = kFc[1 + 0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$, x converged at 0.0072(13). The final refinement gave $R = 0.0470$, $wR = 0.01329$, $S = 1.016$ for 1089 observed reflections. The maximum peak on final ΔF map was 0.875 e/A^3, the minimum -0.756 e/A^3. Crystal data and X-ray details are given in Table 1. Atomic coordinates of non-hydrogen atoms are given in Table 2.

Scheme 1

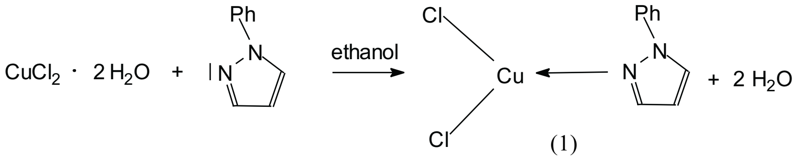

Table 1. Crystal data and structure refinement.

Molecular formula	$Cu_1Cl_2(C_9H_8N_2)$
Molecular weight	278.61
Temperature	293(2)
Radiation	CuKα
Wavelength	1.54178
Crystal system	Triclinic
Space group	$P\,{-1}$
No. of setting reflections	25
Unit cell dimension	$a = 8.534(2)$ Å $b = 10.047(2)$ Å $c = 6.311(2)$ Å $\alpha = 105.21(2)°$ $\beta = 93.45(3)°$ $\gamma = 81.72(2)°$
Volume	$V = 516.6(2)$ Å^3
Z	2
D_x	1.791 g/cm^3
D_m	1.785 g/cm^3 flotation in tetralin & iodomethane
$\mu(CuK_\alpha)$	7.399 mm^{-1}
$F(000)$	293
Crystal size	0.4×0.3×0.3 mm
Diffractometer	AFC5S Rigaku
Scan type	ω scan
No. of standard reflections	3
Decay of standards	< 2%
θ range for data collection	4.60–60.06°
Index ranges	h: 0 → –6, k: –11 → 11, l: –7 → 7
Measured reflections	1446
Independent reflections	1325
Refinement method	Full-matrix least-squares on F^2
Data/parameters	1325/136
Goodness-of-fit	1.016
Final R indices	$R1(\text{on } F) = 0.047$ $wR2(\text{on } F^2) = 0.1349$
Extinction coefficient	0.0072(13)
Largest diff. peak and hole	0.875 , –0.756 e/A^3

Table 2. Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients (Å^2×10^3).

Atom	x	y	z	U(eq)
Cu1	9376(1)	5640(1)	2754(1)	30(1)
Cl1	9514(2)	3584(1)	3756(2)	38(1)
Cl2	8026(2)	4819(1)	–439(2)	35(1)
N12	8838(5)	7631(4)	2681(7)	32(1)
C13	9600(7)	8390(5)	1788(9)	37(1)
C14	8966(8)	9791(5)	2469(10)	45(2)
C15	7768(7)	9838(5)	3775(9)	41(2)
N11	7691(5)	8533(4)	3926(7)	34(1)
C111	6609(6)	8075(5)	5142(9)	34(1)
C112	6538(7)	8628(6)	7366(10)	43(2)
C113	5493(8)	8193(6)	8555(11)	49(2)
C114	4529(7)	7231(6)	7529(10)	48(2)
C115	4589(8)	6700(6)	5258(10)	46(2)
C116	5639(7)	7109(5)	4055(9)	39(1)

The ORTEP [6] drawing of the molecule with the atomic numbering scheme is given in Fig. 1. This work is a continuation of study on Cu^{2+} complexes with phenylpyrazoles [7]. The molecules of the title compound form chains running along *c* axis by di μ-chloro bridges (see Fig. 2). There is a five coordinated Cu^{2+} ion with distorted square-pyramidal (SQP) coordination. The observed SQP coordination is deformed towards trigonal-bipyramidal (TBP) direction. The degree of trigonality $\tau = 0.17$ (see [8] $\tau = 0$ for SQP and $\tau = 1$ for TBP coordination). The basal plane in the polyhedron is defined by N12 atom of phenylpyrazole ligand and the Cl1, Cl2, Cl1^{i} ions [symmetry code (i): –x + 2, –y + 1, –z + 1]. The Cu1–Cl2^{ii} [symmetry code (ii): –x + 2, –y + 1, –z] apical bond completes elongated square-pyramidal (SQP)

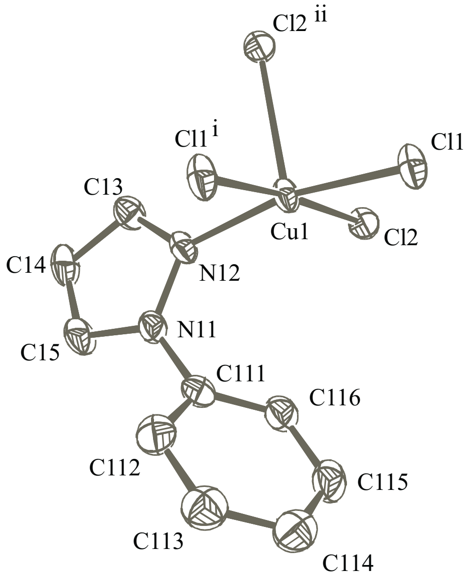

Figure 1. ORTEP drawing of the molecule [symmetry code (i): –x + 2, –y + 1, –z + 1; (ii): –x + 2, –y + 1, –z]. Displacement ellipsoids are drawn at the 40% probability level.

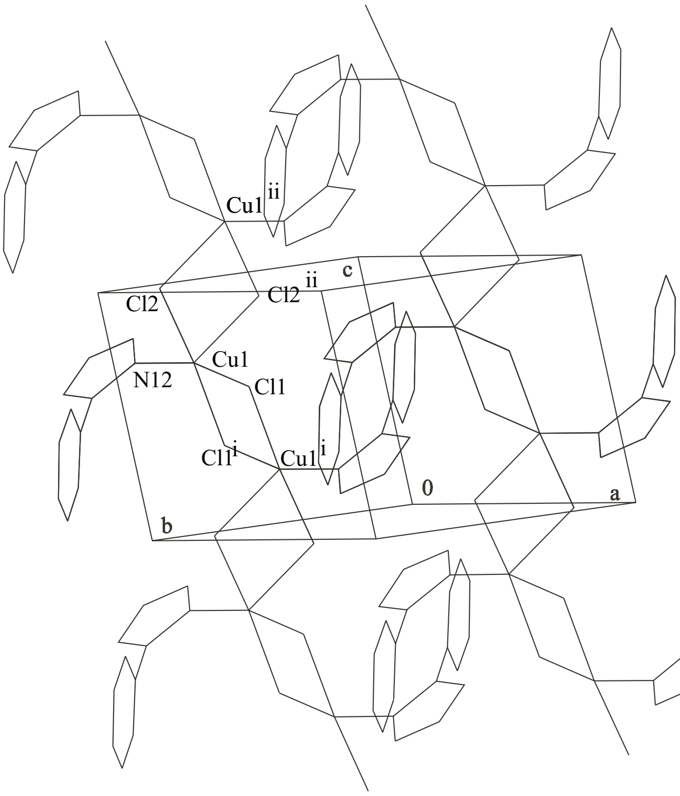

Figure 2. The chains of the molecules with di-μ bridges in the unit cell [symmetry code (i): –x + 2, –y + 1, –z + 1; (ii): –x + 2, –y + 1, –z].

coordinaton. According to bond angles around Cu^{2+} ion the basal plane of SQP is pyramidally distorted [9]. Indeed the deviations of N12, Cl2, Cl1, $Cl1^i$ atoms from their weighted least-squares plane [10] are: –0.231(4), –0.023(1), +0.021(1), +0.026(1) Å respectively and +0.154(1) Å for Cu1. In previous structures the distortion of the basal plane was found to be tetrahedral in dichlorobis(5-phenylpyrazole)copper(II) (compound II) or on the edge between tetrahedral and pyramidal in dichlorobis(3,5-diphenylpyrazole)copper(II) (compound I) [7]. Each two planes defined by the bridges having common Cu^{2+} ion cross at angle 79.4(1)°. In comparison with previous work [7] the five coordinated Cu^{2+} ions show very similar SQP coordination, but the trigonal distortion of the square pyramid seems to be bigger in the previously reported structures [τ (in I) = 0.45, τ (in II) = 0.25]. Observed bond lengths and angles around Cu^{2+} ion and in phenyl, pyrazole rings are in a good agreement with expected values [11,12].

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (no CCDC 160711).

Table 3. Selected bond lengths (Å) and angles (°).

Cu1–N12	2.000(4)	C15–N11	1.351(6)
Cu1–Cl2	2.278(2)	N11–C111	1.430(7)
Cu1–Cl1	2.299(2)	C111–C112	1.369(8)
Cu1–Cl1^{i}	2.328(2)	C111–C116	1.383(8)
Cu1–Cl2^{ii}	2.647(2)	C112–C113	1.383(8)
N12–C13	1.317(7)	C113–C114	1.366(9)
N12–N11	1.364(6)	C114–C115	1.393(8)
C13–C14	1.396(7)	C115–C116	1.378(8)
C14–C15	1.340(8)		
N12–Cu1–Cl2	94.0(1)	N12–C13–C14	110.3(5)
N12–Cu1–Cl1	162.5(1)	C15–C14–C13	105.7(5)
Cl2–Cu1–Cl1	93.0(1)	C14–C15–N11	108.3(5)
N12–Cu1–Cl1^{i}	88.0(1)	C15–N11–N12	109.5(4)
Cl2–Cu1–Cl1^{i}	172.6(1)	C15–N11–C111	128.4(4)
Cl1–Cu1–Cl1^{i}	83.2(1)	N12–N11–C111	122.1(4)
N12–Cu1–Cl2^{ii}	95.1(1)	C112–C111–C116	121.4(6)
Cl2–Cu1–Cl2^{ii}	88.2(1)	C112–C111–N11	118.9(5)
Cl1–Cu1–Cl2^{ii}	101.1(1)	C116–C111–N11	119.8(5)
Cl1^{i}–Cu1–Cl2^{ii}	98.7(1)	C111–C112–C113	119.3(6)
Cu1–Cl1–Cu1^{i}	96.8(1)	C114–C113–C112	120.7(6)
Cu1–Cl2–Cu1^{ii}	91.8(1)	C113–C114–C115	119.4(6)
C13–N12–N11	106.1(4)	C116–C115–C114	120.6(6)
C13–N12–Cu1	129.7(4)	C115–C116–C111	118.7(6)
N11–N12–Cu1	123.4(3)		

Symmetry code (i): –x + 2, –y + 1, –z + 1; (ii): –x + 2, –y + 1, –z.

REFERENCES

1. Nasiadek M., Diploma Thesis, Institute of Chemistry, Faculty of Pharmacy, Medical University of Łódź (1985).
2. TEXSAN: Single Crystal Structure Analysis Software, Ver. 5.0. Molecular Structure Corporation, The Woodlands, TX 77381, (1989b).
3. De Meulenar J. and Tompa H., *Acta Cryst.*, **19**, 1014 (1965).
4. Sheldrick G.M., SHELXS-86. Program for the Solution of Crystal Structures. Univ. of Göttingen, Germany (1990).
5. Sheldrick G.M., SHELXL97. Program for the Refinement of Crystal Structures. Univ. of Göttingen, Germany (1997).
6. Mc Ardle P., ORTEX V3.1a, *J. Appl. Cryst.*, **28**, 65 (1995).
7. Małecka M., Grabowski M.J., Olszak T.A., Kostka K. and Strawiak M., *Acta Cryst.*, **C54**, 1770 (1998).
8. Addison A.W., Nageswara Rao T., Reedijk J., van Rijn J. and Verschoor G.C., *J. Chem. Soc. Dalton Trans.*, 1349 (1984).
9. Bukowska-Strzyżewska M., Maniukiewicz W. and Sieroń L., *Acta Cryst.*, **B53** 466 (1997).
10. Nardelli M., *J. Appl. Cryst.*, **29**, 296 (1996).
11. Allen F.H., Kennard O., Watson D.G., Brammer L., Orpen A.G. and Taylor R., *J. Chem. Soc. Perkin. Trans*. 2, pp. S1–S19 (1987).
12. Orpen A.G., Brammer L., Allen F.H., Kennard O., Watson D.G. and Taylor R., *J. Chem. Soc. Dalton Trans*., pp. S1–S83 (1989).