

Dichlorotetrakis(3-phenylpyrazole- κN^2)-copper(II)

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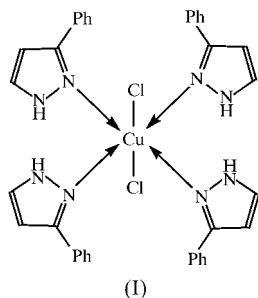
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In the title compound, $[\text{CuCl}_2(\text{C}_9\text{H}_8\text{N}_2)_4]$, there are two independent molecules in the asymmetric unit. The Cu^{2+} ions lie on inversion centres and are octahedrally coordinated by two Cl atoms and four pyrazole N atoms. All pyrazole N–H groups form intramolecular hydrogen bonds, giving rise to five-membered hydrogen-bonded rings incorporating the Cu atoms.

Comment

This paper is a continuation of our X-ray crystal structure studies on copper(II) chloride complexes incorporating phenylpyrazole ligands (Małecka *et al.*, 1998, 2001). This group of complexes is of interest because of their expected biological activities as fungicides and herbicides (Nasiadek, 1985). Previous studies on copper(II) complexes with different substituted pyrazoles were undertaken with regard to their protolytic properties and the influence of the nature and position of substituents on metal complexation (Kostka & Strawiak, 1982; Goslar *et al.*, 1987, 1988). On the other hand, we are investigating nitrogen-containing heterocyclic ligands and their complexes because of the expected pharmacological activity, by analogy to *cis*-platinum complexes (Hollis, 1989; Reedijk, 1996).



The X-ray structure analysis of the title complex, (I), was carried out in order to elucidate both the geometry around the Cu^{2+} ion and the packing arrangement in the crystal, which is often related to the coordination ability towards transition metal ions (Ochocki *et al.*, 1998).

Compound (I) crystallizes with two crystallographically independent centrosymmetric molecules, *A* and *B*, in the asymmetric unit, with the two Cu^{2+} ions located on the centres of symmetry at $(0, 0, 0)$ and $(\frac{1}{2}, 0, \frac{1}{2})$, respectively.

The metal coordination polyhedron is an elongated octahedral bipyramid with two Cl^- ions in *trans*-apical positions and four pyrazole N atoms forming the equatorial plane. The

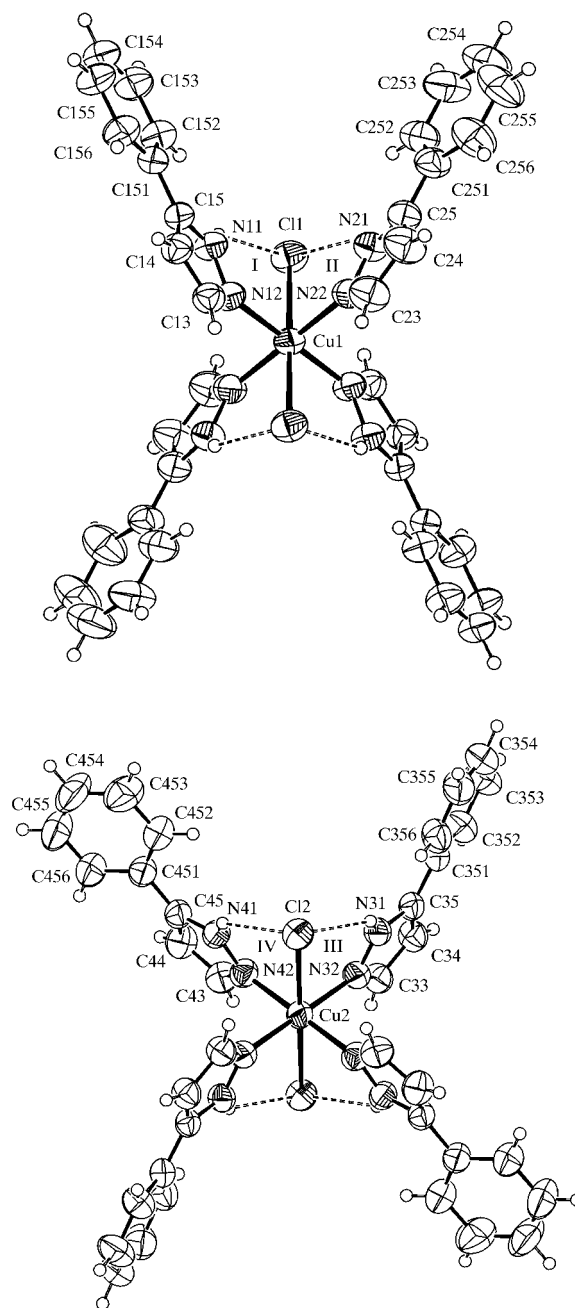


Figure 1

Views of molecules *A* (top) and *B* (bottom), showing the atom-numbering schemes and the intramolecular hydrogen bonds (dashed lines) which give rise to five-membered hydrogen-bonded rings I, II, III and IV. All H atoms, except for H11, H21, H31 and H41 (shown as spheres), have been omitted for clarity. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

Cl—Cu—Cl lines deviate by 2.19 (6) and 2.58 (7)° from being orthogonal to these equatorial planes for molecules *A* and *B*, respectively.

In the two independent molecules, some differences are observed with regard to the rotation of the phenyl and pyrazole rings about the *Cn5*—*Cn51* bond joining them, as shown by the *Nn1*—*Cn5*—*Cn51*—*Cn52* (*n* = 1–4) torsion angles (see Table 1).

The orientation of the pyrazole ligands around the metal ions is not the same in the two independent molecules, as indicated by the Cl—Cu—N—N torsion angles. The different distortions of the ligands in molecules *A* and *B* can be explained by the different packing interactions. These interactions are of the C—H···Cl and C—H···C_g types (C_g are the centroids of pyrazole rings *Nn1*/*Nn2*/*Cn3*/*Cn4*/*Cn5*, where *n* = 2 and 3). The geometry for these weak interactions is given in Table 2.

Two intramolecular hydrogen bonds are observed in each molecule, producing four five-membered hydrogen-bonded rings, incorporating the Cu atoms (see Fig. 1), which adopt the following conformations: H11-envelope for ring I, twisted for rings II and IV, and N31-half-chair for ring III. The puckering parameters (Cremer & Pople, 1975) corresponding to the Cu—*Nn2*—*Nn1*—*Hn1*···Cl (*n* = 1–4) atom sequences are $q_2 = 0.11$ (1) Å and $\varphi_2 = 65$ (2)°, $q_2 = 0.18$ (1) Å and $\varphi_2 = -142$ (1)°, $q_2 = 0.28$ (1) Å and $\varphi_2 = 19$ (1)°, and $q_2 = 0.19$ (1) Å and $\varphi_2 = -144$ (1)° for rings I, II, III and IV, respectively.

The bond distances and angles in both molecules are in good agreement with expected values (Allen *et al.*, 1987).

Experimental

The title compound was obtained by mixing hot ethanol solutions of CuCl₂·2H₂O and 5-phenylpyrazole in a 1:4 molar ratio. On cooling to room temperature, a crystalline material began to separate. This material was filtered off and washed three times with cold solvent and dried *in vacuo* over phosphorus pentoxide, giving single crystals of the title compound suitable for X-ray analysis.

Crystal data

[CuCl ₂ (C ₉ H ₈ N ₂) ₄]	$D_m = 1.356$ Mg m ⁻³
$M_r = 711.14$	D_m measured by flotation in tetralin and iodomethane
Triclinic, $P\bar{1}$	Cu $K\alpha$ radiation
$a = 11.587$ (4) Å	Cell parameters from 22 reflections
$b = 12.676$ (3) Å	$\theta = 23.0$ – 31.9°
$c = 13.352$ (3) Å	$\mu = 2.60$ mm ⁻¹
$\alpha = 81.54$ (2)°	$T = 293$ (2) K
$\beta = 72.71$ (2)°	Prism, blue
$\gamma = 68.29$ (2)°	$0.60 \times 0.50 \times 0.25$ mm
$V = 1738.1$ (9) Å ³	
$Z = 2$	
$D_x = 1.359$ Mg m ⁻³	

Data collection

Rigaku AFC-5S diffractometer	$R_{int} = 0.028$
ω scans	$\theta_{max} = 67.5^\circ$
Absorption correction: analytical (de Meulenaer & Tompa, 1965)	$h = -13 \rightarrow 13$
$T_{min} = 0.296$, $T_{max} = 0.569$	$k = -15 \rightarrow 11$
6374 measured reflections	$l = -15 \rightarrow 15$
6079 independent reflections	3 standard reflections
4962 reflections with $I > 2\sigma(I)$	every 150 reflections
	intensity decay: <2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0958P)^2 + 0.0725P]$
$R[F^2 > 2\sigma(F^2)] = 0.047$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.152$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.14$	$\Delta\rho_{max} = 0.41$ e Å ⁻³
6079 reflections	$\Delta\rho_{min} = -0.65$ e Å ⁻³
432 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.0275 (12)

Table 1

Selected geometric parameters (Å, °).

Cu1—N12	1.998 (2)	Cu2—N42	1.993 (2)
Cu1—N22	2.027 (2)	Cu2—N32	2.026 (2)
Cu1—Cl1	2.8174 (10)	Cu2—Cl2	2.8226 (10)
N12—Cu1—N22	87.39 (10)	N42—Cu2—N32	90.10 (9)
N12—Cu1—Cl1	88.90 (7)	N42—Cu2—Cl2	88.92 (7)
N22—Cu1—Cl1	88.1 (2)	N32 ⁱ —Cu2—Cl2	92.35 (7)
Cl1—Cu1—N12—N11	1.0 (2)	Cl2—Cu2—N32—N31	-15.8 (2)
N11—C15—C151—C152	-0.6 (4)	N31—C35—C351—C352	-148.2 (3)
Cl1—Cu1—N22—N21	5.7 (2)	Cl2—Cu2—N42—N41	6.5 (2)
N21—C25—C251—C252	-10.1 (5)	N41—C45—C451—C452	12.9 (4)

Symmetry code: (i) $1 - x, -y, 1 - z$.

Table 2

Hydrogen-bonding geometry (Å, °).

C_g2 and C_g3 are the centroids of the N21- and N31-containing pyrazole rings, respectively.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N11—H11···Cl1	0.86	2.40	3.071 (2)	135
N21—H21···Cl1	0.86	2.41	3.081 (3)	135
N31—H31···Cl2	0.86	2.47	3.120 (3)	133
N41—H41···Cl2	0.86	2.41	3.084 (2)	135
C14—H14···Cl2 ⁱ	0.93	2.93	3.805 (3)	158
C155—H155···Cl2 ⁱⁱ	0.93	2.85	3.707 (4)	154
C13—H13···C _g 3 ⁱ	0.93	2.90	3.638 (5)	137
C455—H455···C _g 3 ⁱⁱⁱ	0.93	2.88	3.693 (6)	146
C456—H456···C _g 2 ^{iv}	0.93	2.87	3.670 (5)	144

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

All H atoms were positioned geometrically (N—H = 0.86 Å and C—H = 0.93 Å) and refined with a riding model. For the H atoms of the phenyl and pyrazole rings (except for the H atoms of the N—H groups), U_{iso} values were constrained to be 1.2 U_{eq} of the carrier atom. The H atoms of the N—H groups were placed in calculated positions and their U_{iso} values were refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1998); software used to prepare material for publication: *PARST97* (Nardelli, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1596). Services for accessing these data are described at the back of the journal.

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