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Investigations of Complexes of Copper(II) Chloride with Phenylpyrazoles

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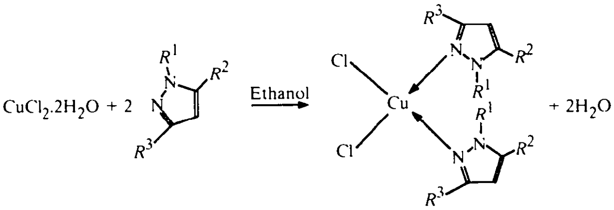
Abstract

The crystal structures of dichlorobis(3,5-diphenylpyrazole-N^2)copper(II), [$CuCl_2(C_{15}H_{12}N_2)_2$], (I), dichlorobis(5-phenylpyrazole-N^2)copper(II), [$CuCl_2(C_9H_8N_2)_2$], (II), and dichlorobis(1-phenylpyrazole-N^2)copper(II), [$CuCl_2(C_9H_8N_2)_2$], (III), have been determined from X-ray diffraction data. There are significant differences in the coordination of the Cl^- ions to the Cu^{2+} ion. The coordination of the Cu^{2+} ion is distorted square pyramidal in compounds (I) and (II), and distorted tetrahedral in (III). All available N—H groups form hydrogen bonds, which are intra- and intermolecular in (I), and intramolecular in (II). An N—H group in (I) forms a bifurcated hydrogen bond. Intermolecular intereactions between neighbouring molecules form dimers and chains in (I) and (II), respectively.

Comment

This paper deals with X-ray crystal structure studies on copper(II) chloride complexes of phenylpyrazoles. Previous studies on copper(II)-substituted pyrazole complexes were undertaken on their protolitic properties and on the influence of the nature and position of substituents on metal complexation (Kostka & Strawiak, 1982; Goslar *et al.*, 1987, 1988; Nasiadek, 1985). The X-ray structure analyses of dichlorobis(3,5-diphenylpyrazole)copper(II), (I), dichlorobis(5-phenylpyrazole)copper(II), (II), and dichlorobis(1-phenylpyrazole)copper(II), (III), were undertaken to elucidate the geometry around the Cu^{2+} ion.



(I) R^1 = H; R^2 = R^3 = Ph
(II) R^1 = R^3 = H : R^2 = Ph
(III) R^1 = Ph: R^2 = R^3 = H

In (I), there is a five-coordinated Cu^{2+} ion with distorted square-pyramidal coordination. The basal plane is defined by two *cis*-N atoms of two phenylpyrazole ligands and two Cl^- ions, with the apical Cl1^{i} ligand being shared by two adjacent complexes [symmetry code: (i) $-x$, $1-y$, $-z$]; thus, the molecules form dimers. Moreover, an intermolecular N21—H21···Cl2^{i} hydrogen bond also leads to dimerization. The N21 atom is also involved in an intramolecular N21—H21···Cl1 hydrogen bond, but this three-centre interaction is weak, as indicated by the long H···Cl distances. A stronger intramolecular hydrogen bond is formed by the H11 atom (N11—H11···Cl2; see Table 2 and Fig. 1). The base of the distorted square pyramid is not planar; the deviations of the N12, N22, Cl1 and Cl2 atoms from their weighted least-squares plane (Nardelli, 1996) are −0.374 (3), 0.530 (4), −0.038 (1) and 0.052 (1) Å, respectively, and −0.226 (1) Å for Cu1. The C255 atom is disordered over two positions, the most populated site having an occupation factor of 0.68 (5).

In (II), the geometry around the Cu^{2+} ion is best described as square pyramidal with the basal plane formed by the two *trans*-N atoms of the phenylpyrazole ligands and two Cl^- ions; the fifth apical site is occupied by one Cl^{ii} ion from a neighbouring molecule [symmetry code: (ii) $x-\frac{1}{2}$, $\frac{1}{2}-y$, z]. Thus, the molecules form chains running along the *a* axis. The base of the pyramid is not planar; the deviations of the N12, Cl1, N22 and Cl2 atoms from their weighted least-squares plane (Nardelli, 1996) are 0.463 (4), −0.050 (1), 0.451 (4) and −0.062 (1) Å, respectively, with Cu1 displaced by 0.359 (1) Å. The N11 and N21 atoms form intramolecular hydrogen bonds (N11—H11···Cl2 and N21—H21···Cl2; see Table 4 and Fig. 2).

In (III) (Fig. 3), the four-coordinated Cu^{2+} ion lies on a twofold axis, with a distorted tetrahedral geometry, being bonded to two Cl^- ions and two N atoms of two phenylpyrazole ligands. The dihedral angle between the N12/Cu1/Cl1 plane and its symmetry related plane at $(2-x, 1-y, z)$ is 123.0 (1)°.

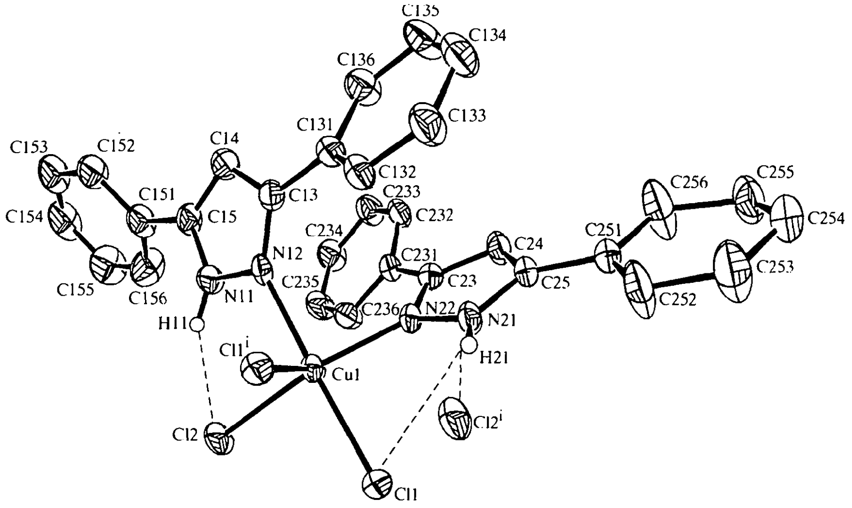


Fig. 1. The molecular structure and atomic numbering scheme of compound (I) [only the major occupancy C255 atom is shown; occupancy 0.68 (5)]. Displacement ellipsoids are drawn at the 40% probability level. [Symmetry code: (i) $-x, 1-y, -z$.]

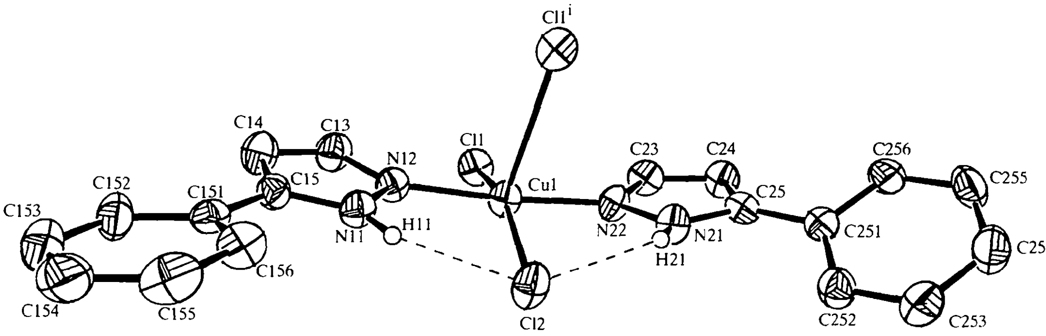


Fig. 2. The molecular structure and atomic numbering scheme of compound (II). Displacement ellipsoids are drawn at the 40% probability level. [Symmetry code: (ii) $x-\frac{1}{2}, \frac{1}{2}-y, z$.]

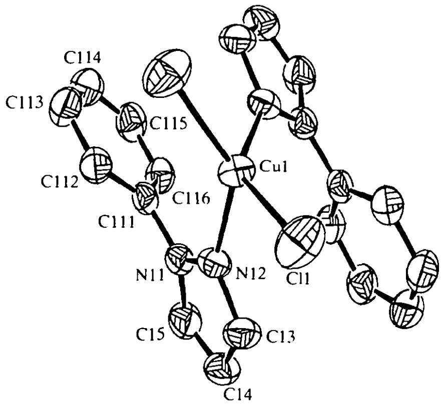


Fig. 3. The molecular structure and atomic numbering scheme of compound (III). Displacement ellipsoids are drawn at the 40% probability level.

Bond distances and angles in the phenyl and pyrazole rings of the three structures are in good agreement with expected values (Allen *et al.*, 1987; Orpen *et al.*, 1989).

Experimental

The title compounds were obtained according to Nasiadek (1985) by mixing hot ethanolic solutions of $CuCl_2.2H_2O$ and the appropriate phenylpyrazole in a molar ratio of 1:2. On cooling to room temperature, the crystalline compounds began to separate. The complexes were filtered and washed three times with cold solvent and dried *in vacuo* over phosphorus pentaoxide.

Compound (I)

Crystal data

$[CuCl_2(C_{15}H_{12}N_2)_2]$
$M_r = 574.97$

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å

Monoclinic
$P2_1/n$
$a = 13.380\ (2)$ Å
$b = 15.140\ (3)$ Å
$c = 13.634\ (1)$ Å
$\beta = 109.46\ (1)°$
$V = 2604.1\ (7)$ Å^3
$Z = 4$
$D_x = 1.467$ Mg m^{-3}
$D_m = 1.469$ Mg m^{-3}
D_m measured by flotation in tetralin/iodomethane

Cell parameters from 25 reflections
$\theta = 36.18–39.87°$
$\mu = 3.302$ mm^{-1}
$T = 293\ (2)$ K
Plate
0.30 × 0.15 × 0.10 mm
Brown

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
$T_{\min} = 0.525$, $T_{\max} = 0.737$
4053 measured reflections
3868 independent reflections

2633 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.032$
$\theta_{\max} = 60.09°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 17$
$l = -15 \rightarrow 14$
3 standard reflections every 150 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.119$
$S = 0.896$
3868 reflections
366 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0740P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.021$
$\Delta\rho_{\max} = 0.648$ e Å^{-3}
$\Delta\rho_{\min} = -0.667$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00017 (10)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (I)*

Cu1—N22	2.011 (3)	Cu1—Cl2	2.327 (1)
Cu1—N12	2.040 (3)	Cu1—Cl1$^{\rm i}$	2.587 (1)
Cu1—Cl1	2.297 (1)		
N22—Cu1—N12	89.96 (12)	Cl1—Cu1—Cl2	89.46 (4)
N22—Cu1—Cl1	87.97 (9)	N22—Cu1—Cl1$^{\rm i}$	114.74 (10)
N12—Cu1—Cl1	177.92 (9)	N12—Cu1—Cl1$^{\rm i}$	92.80 (9)
N22—Cu1—Cl2	151.03 (11)	Cl1—Cu1—Cl1$^{\rm i}$	87.85 (4)
N12—Cu1—Cl2	92.47 (9)	Cl2—Cu1—Cl1$^{\rm i}$	93.97 (4)

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

Table 2. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11···Cl2	0.89 (4)	2.22 (4)	2.971 (4)	142 (3)
N21—H21···Cl1	0.93 (5)	2.93 (5)	3.220 (3)	100 (3)
N21—H21···Cl2$^{\rm i}$	0.93 (5)	2.52 (5)	3.441 (4)	174 (4)

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

Compound (II)

Crystal data

[$CuCl_2(C_9H_8N_2)_2$]
$M_r = 422.79$

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å

Monoclinic
$P2_1/a$
$a = 8.041\ (2)$ Å
$b = 15.768\ (3)$ Å
$c = 14.549\ (2)$ Å
$\beta = 91.73\ (2)°$
$V = 1843.7\ (7)$ Å^3
$Z = 4$
$D_x = 1.523$ Mg m^{-3}
$D_m = 1.635$ Mg m^{-3}
D_m measured by flotation in tetralin/iodomethane

Cell parameters from 25 reflections
$\theta = 23.00–28.63°$
$\mu = 4.398$ mm^{-1}
$T = 293\ (2)$ K
Needle
0.40 × 0.16 × 0.10 mm
Green

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
$T_{\min} = 0.204$, $T_{\max} = 0.659$
2963 measured reflections
2736 independent reflections

1632 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.082$
$\theta_{\max} = 60.07°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 17$
$l = -16 \rightarrow 16$
3 standard reflections every 150 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.110$
$S = 0.824$
2736 reflections
246 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0536P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.017$
$\Delta\rho_{\max} = 0.402$ e Å^{-3}
$\Delta\rho_{\min} = -0.418$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00002 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (II)*

Cu1—N12	1.995 (4)	Cu1—Cl2	2.3211 (15)
Cu1—N22	2.003 (4)	Cu1—Cl1$^{\rm i}$	2.8741 (16)
Cu1—Cl1	2.2675 (14)		
N12—Cu1—N22	174.3 (2)	Cl1—Cu1—Cl2	159.2 (1)
N12—Cu1—Cl1	91.6 (1)	N12—Cu1—Cl1$^{\rm i}$	92.4 (1)
N22—Cu1—Cl1	90.2 (1)	Cl1—Cu1—Cl1$^{\rm i}$	105.6 (1)
N12—Cu1—Cl2	89.6 (1)	N22—Cu1—Cl1$^{\rm i}$	81.9 (1)
N22—Cu1—Cl2	90.6 (1)	Cl2—Cu1—Cl1$^{\rm i}$	95.1 (1)

Symmetry code: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z$.

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11···Cl2	0.78 (5)	2.32 (5)	2.981 (4)	143 (5)
N21—H21···Cl2	0.89 (5)	2.35 (5)	2.994 (4)	129 (4)

Compound (III)

Crystal data

[$CuCl_2(C_9H_8N_2)_2$]
$M_r = 422.79$

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å

Tetragonal
$I4_1cd$
$a = 14.795$ (1) Å
$c = 16.634$ (2) Å
$V = 3641.2$ (6) Å^3
$Z = 8$
$D_x = 1.542$ Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 31.59$–$39.73°$
$\mu = 4.454$ mm^{-1}
$T = 293$ (2) K
Prism
0.40 × 0.16 × 0.10 mm
Brown–red

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
$T_{\min} = 0.318$, $T_{\max} = 0.634$
9986 measured reflections
1354 independent reflections

1099 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.070$
$\theta_{\max} = 60.07°$
$h = -16 \rightarrow 16$
$k = -16 \rightarrow 16$
$l = -18 \rightarrow 18$
3 standard reflections every 150 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.063$
$S = 0.923$
1354 reflections
122 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0432P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.010$
$\Delta\rho_{\max} = 0.229$ e Å^{-3}
$\Delta\rho_{\min} = -0.206$ e Å^{-3}

Extinction correction: *SHELXL97*
Extinction coefficient: 0.00015 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.01 (2)

Table 5. *Selected geometric parameters (Å, °) for (III)*

Cu1—N12	2.020 (3)	Cu1—Cl1	2.214 (1)
N12—Cu1—N12$^{\rm i}$	97.73 (15)	N12—Cu1—Cl1	96.12 (8)
N12—Cu1—Cl1$^{\rm i}$	138.42 (8)	Cl1$^{\rm i}$—Cu1—Cl1	98.97 (7)

Symmetry code: (i) $2 - x, 1 - y, z$.

For all compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989*a*); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989*b*); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEX3.1a* (McArdle, 1995); software used to prepare material for publication: *PARST97* (Nardelli, 1996).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1369). Services for accessing these data are described at the back of the journal.

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Bis(dimethylammonium) Pentachloroantimonate(III), on the Deformation of the Octahedral Coordination of Sb$^{\rm III}$

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Abstract

The structure of the title compound, $[NH_2(CH_3)_2]_2[SbCl_5]$, was determined at 295 and 85 K. It consists of polymeric $(SbCl_5^{2-})_n$ chains composed of deformed $SbCl_6^{3-}$ octahedra connected by corners and dimethylammonium cations. The temperature dependence of the Sb—Cl bond lengths is discussed. It is argued that the deformation of the octahedral coordination of the Sb$^{\rm III}$ atom is caused by electrostatic interaction/hydrogen bonds.

Comment

Alkylammonium chloroantimonates are obtained by mixing amine hydrochloride and antimony trichloride in an organic solvent or aqueous hydrochloric acid. Depending on the ratio of the reactants used, the type of cation, the solvent and the experimental conditions one or more products of different stoichiometries may be obtained. They are defined by the general formula $R_aSb_bCl_c$ (R = alkylammonium cation, $c = 3b + a$). These compounds are attracting growing attention since many salts of this group undergo numerous phase tran-