metal-organic papers

Dichlorotetrakis(1H-pyrazole-κN^2)copper(II)

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The reaction of $CuCl_2$ and pyrazole (Hpz) in methanol solution at room temperature yields the title mononuclear complex, $[CuCl_2(C_3H_4N_2)_4]$. The Cu atom is six-coordinated by four N atoms from four pyrazole ligands and by two Cl^- ions. The overall symmetry of the complex is $\bar{1}$. The structure features N—H···Cl and C—H···Cl hydrogen bonds, yielding a three-dimensional network.

Comment

Since Trofimenko discovered poly(pyrazolyl)borate in 1966 (Trofimenko, 1972), the coordination chemistry of pyrazole ligands has attracted much attention (Li *et al.*, 2004; Trofimenko, 1993; Mukheerjee, 2000). The donor N atom of pyrazole can coordinate to metal atoms and the other N atom often forms hydrogen bonds with other atoms in the complexes, acting as either a hydrogen-bond donor or acceptor. Based on these findings, we attempted to determine the structure of the title complex, $Cu(pyrazole)_4Cl_2$. (I).

(I)
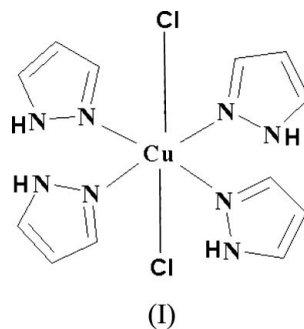
The structure of (I) features a distorted octahedral complex of Cu^{2+}, which is coordinated in a square-planar fashion by four N atoms from four pyrazole ligands and two axial Cl^- ligands (Fig. 1). The Cu atom is located on a special position (site symmetry $\bar{1}$). Selected bond lengths and angles are listed in Table 1.

The Cu—N distances of 2.001 (3) and 2.025 (3) Å are significantly longer than those in $[Cu(Hpz)_4SO_4](H_2O)$ [mean 1.944 (6) Å; Shen *et al.*, 2004] or $[Cu_3(\mu_3\text{-}O)(pz)_3(Hpz)_3(\mu_1,\mu_2\text{-}ClO_4)](CH_3OH)$ [mean 1.982 (5) Å; Shen *et al.*, 2004], but are close to the bond lengths found in $[Cu(Hpz)_4SO_4]_n(CH_3OH)_n$ [mean 2.016 (3) Å; Shen *et al.*, 2004]. The Cu···Cl distance of 2.839 (10) Å corresponds to a rather weak Cu—Cl bond. The *cis*-N—Cu—N angles deviate only slightly from 90° (Table 1). The Cu1—N1—N2—C3 and Cu1—N3—N4—C6 torsion angles are −179.2 (3) and 173.0 (3)°, respectively.
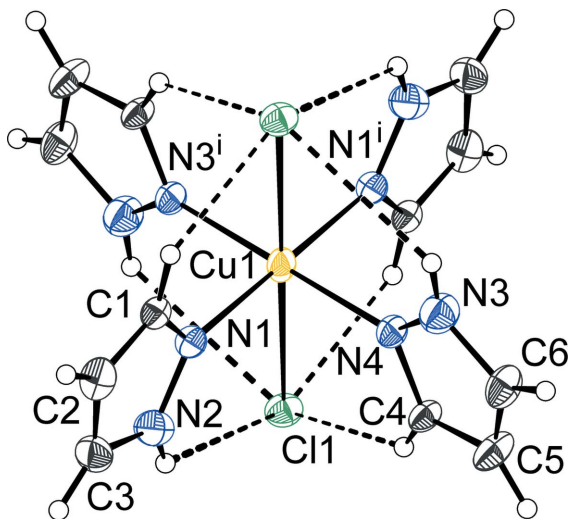
Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level. Unlabelled atoms and those labelled with a superscript i are related to labelled atoms by the symmetry code ($\frac{1}{2} - x$, $\frac{1}{2} - y$, $1 - z$). Hydrogen bonds are drawn as dashed lines.

Two kinds of hydrogen bond are present in the structure of (I) (Fig. 2 and Table 2). Firstly, there are hydrogen bonds between uncoordinated N atoms and the Cl atoms, and secondly there are hydrogen bonds between C atoms of the pyrazole ring and Cl atoms. Together, these hydrogen bonds yield a chain along the *ac* plane and the chains are further extended into a three-dimensional network in space.

Experimental

The starting materials were purchased from a commercial source (J & K CHEMICAL) and used without further purification. A methanol solution (10 ml) of $CuCl_2$ (0.190 g) and pyrazole ($C_3H_4N_2$) (0.536 g) was stirred for 4 h at room temperature, yielding a blue solution. This was set aside to crystallize, yielding analytically pure (I) as single crystals suitable for X-ray structure determination. Analysis, found: C 35.32, H 3.87, N 27.56%; calculated for $C_{12}H_{16}Cl_2Cu_1N_8$: C 35.40, H 3.93, N 27.53%.

Crystal data

$[CuCl_2(C_3H_4N_2)_4]$	$Z = 4$
$M_r = 406.77$	$D_x = 1.637$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 13.674$ (8) Å	$\mu = 1.66$ mm^{-1}
$b = 9.172$ (5) Å	$T = 293$ (2) K
$c = 14.750$ (8) Å	Block, blue
$\beta = 116.852$ (9)°	$0.23 \times 0.20 \times 0.15$ mm
$V = 1650.5$ (16) Å^3	

Data collection

Bruker APEXII diffractometer	4803 measured reflections
ω scans	1710 independent reflections
Absorption correction: multi-scan	1603 reflections with $I > 2\sigma(I)$
(*SADABS*; Sheldrick, 2003)	$R_{int} = 0.041$
$T_{min} = 0.690$, $T_{max} = 0.847$	$\theta_{max} = 26.5°$
(expected range = 0.635–0.780)	
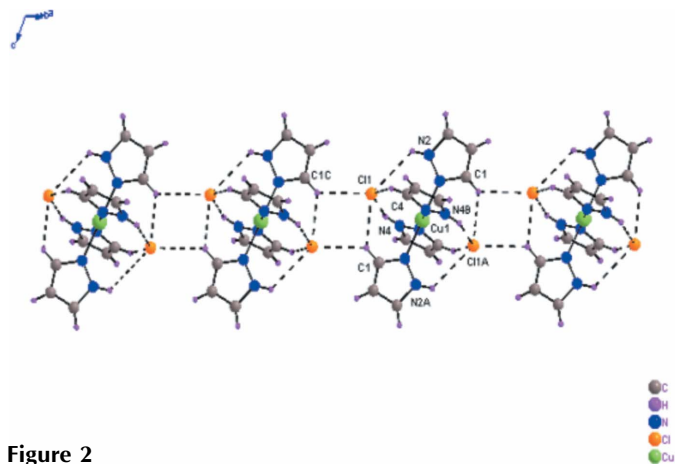
Figure 2
The two-dimensional hydrogen-bond structure along the *ac* plane in (I). [Symmetry codes: (A) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (B) x, y, z; (C) $x - \frac{1}{2}, y - \frac{1}{2}, z$.]

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0886P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.049$	$+ 4.2919P]$
$wR(F^2) = 0.159$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.17$	$(\Delta/\sigma)_{max} = 0.001$
1710 reflections	$\Delta\rho_{max} = 0.72$ e Å^{-3}
106 parameters	$\Delta\rho_{min} = -0.71$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cu1—N3	2.001 (3)	Cu1—Cl1	2.8386 (15)
Cu1—N1	2.025 (3)		
N3^i—Cu1—N1	91.40 (12)	N3—Cu1—N1	88.60 (12)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C1—H1$A\cdots$Cl1^i	0.93	2.53	3.211 (4)	130
C1—H1$A\cdots$Cl1^{ii}	0.93	2.77	3.479 (5)	133
N2—H2$A\cdots$Cl1	0.86	2.89	3.467 (5)	126
N2—H2$A\cdots$Cl1^{iii}	0.86	2.95	3.646 (5)	139

Symmetry codes: (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (ii) $x + \frac{1}{2}, y + \frac{1}{2}, z$; (iii) $-x, y, -z + \frac{1}{2}$.

H atoms were placed in calculated positions and constrained to ride on their parent C atoms, with C—H = 0.93 Å and N—H = 0.86 Å, and with $U_{iso}(H) = 1.2U_{iso}(C,N)$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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