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Dichlorido[(3,5-dimethyl-1*H*-pyrazol-1-yl)methane]copper(II)

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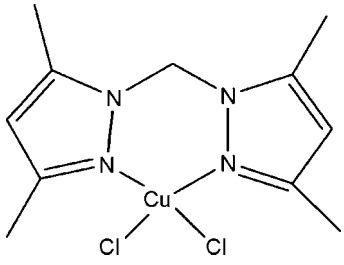
Key indicators: single-crystal X-ray study; T = 193 K; mean σ(C–C) = 0.004 Å; R factor = 0.030; wR factor = 0.075; data-to-parameter ratio = 16.7.

The title compound, $[CuCl_2(C_{11}H_{16}N_4)]$, is isostructural with the previously characterized Zn^{II} analogous complex. The Cu^{II} ion is four-coordinate in a $CuCl_2N_2$ distorted tetrahedral geometry. In the crystal structure, weak C—H···Cl interactions are observed.

Related literature

For details of the antitumour activity of pyrazole-containing complexes, see: Ciesielska *et al.* (2006). For the dimethylpyrazole derivative used as a ligand, see: Rüfenacht (1973). The title complex is isostructural with the Zn analogue (Cheng *et al.*, 2006). For the Cambridge Structural Database, used for comparison with other complexes containing a $[CuCl_2N_2]$ core, see: Allen (2002).



Experimental

Crystal data

$[CuCl_2(C_{11}H_{16}N_4)]$
M_r = 338.72
Monoclinic, $C2/c$
a = 14.8120 (7) Å
b = 16.7384 (9) Å
c = 12.4943 (6) Å
β = 113.58 (1)°
V = 2839.0 (3) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 1.90 mm^{-1}
T = 193 (2) K
0.2 × 0.1 × 0.1 mm

Data collection

Stoe IPDSII diffractometer
Absorption correction: none
39701 measured reflections
2790 independent reflections
2619 reflections with $I > 2\sigma(I)$

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.075
S = 1.11
2790 reflections
167 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1B···Cl3^{i}	0.99	2.75	3.674 (2)	155
C6—H6C···Cl3^{ii}	0.98	2.87	3.676 (3)	140
C11—H11B···Cl3^{iii}	0.98	2.84	3.692 (3)	146
C11—H11C···Cl3^{iv}	0.98	2.85	3.714 (2)	147

Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $x, -y+1, z-\frac{1}{2}$; (iii) $x, -y+1, z+\frac{1}{2}$; (iv) $-x, y, -z+\frac{3}{2}$.

Data collection: *IPDS2* (Stoe & Cie, 2000); cell refinement: *IPDS2*; data reduction: *IPDS2*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PARST97* (Nardelli, 1996).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BH2127).

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supplementary materials

Acta Cryst. (2007). E**63**, m2782 [**doi:10.1107/S1600536807048878**]

Dichlorido[(3,5-dimethyl-1*H*-pyrazol-1-yl)methane]copper(II)

K. Malinowska and R. Modranka

Comment

There have been numerous attempts to improve the effectiveness of antitumor agent *cis*-platin, through the modification of its structure. A number of pyrazole and its derivatives complexes were studied with respect to their cytotoxicity, apoptosis induction ability, and DNA damaging (Ciesielska *et al.*, 2006). While searching for new complexes with ligands similar to previously studied ones, we synthesized a new Cu^{II} complex including a dimethylpyrazole derivative as ligand, (I).

Complex (I) is isostructural with the Zn^{II} analogue, dichloro[(3,5-dimethyl-1*H*-pyrazol-1-yl)methane]zinc(II), reported by Cheng *et al.* (2006). Ionic radii for Cu^{II} and Zn^{II}, 0.069 and 0.074 nm respectively, compare well, allowing isomorphous compounds to be formed.

In (I), the Cu^{II} ion is four coordinated by two N atoms and two Cl atoms (Fig. 1). This $[CuCl_2N_2]$ coordination environment forms a distorted tetrahedral geometry with local non-crystallographic C_s symmetry. Angles around the Cu^{II} ion range from 115.28 (6) to 89.30 (8)°. These angles are comparable with those observed in other $[CuCl_2N_2]$ coordination spheres (CSD, Version 5.28; Allen, 2002). The range of angles are 97.43–128.52° and 78.95–142.27° for Cl—Cu—Cl and N—Cu—N fragments, respectively (333 observations). The Cu—Cl and Cu—N bond lengths in (I) are also comparables with those observed in $[CuCl_2N_2]$ moieties, which have averages of 2.22 and 2.05 Å, respectively, in the CSD.

In the crystal structure of (I) there are extensive C—H···Cl interactions (Table 2, Fig. 2). On the other hand, heterocyclic rings N1/N2/C2/C3/C4 in the asymmetric unit and N3/N4/C7/C8/C9 at position (1/2 − *x*, 1 − *y*, 1 − *z*) interact through π–π stacking interactions. The interplanar spacing is 3.531 (2) Å, while centroids of the rings are separated by 3.508 Å. The ring N3···C9 also interacts with a symmetry related N3···C9 ring at (1/2 − *x*, 1/2 − *y*, 2 − *z*). The interplanar spacing is 3.651 (2) Å, while the centroid to centroid separation is 3.650 Å.

Experimental

The title compound was obtained by reaction of *N*-hydroxymethyl-3,5-dimethylpyrazole (Rüfenacht, 1973) with $CuCl_2$ (2:1 stoichiometric ratio) in ethanol at room temperature. Crystals were obtained by slow evaporation at room temperature. The product (green needles) was obtained in 52% yield.

Refinement

The crystal used for data collection revealed to be twinned, and a twin-integration based on two orientations was done. A first refinement was carried out using HKLF 5 option in *SHELXL*97 (Sheldrick, 1997), resulting in a twin ratio 0.241 (2)/0.759 (2). Option LIST 6 was then applied in order to get a structure factors file containing merged data for a non-twinned model and the structure was refined to convergence. All H atoms were positioned geometrically and refined with a riding model; for methyl H atoms U_{iso} were constrained to be 1.5 times U_{eq} of the carrier atom and C—H = 0.98 Å; for others H atoms U_{iso}

were constrained to be 1.2 times U_{eq} of the carrier atom and C—H = 0.97, 0.93, 0.86 or 0.82 Å for methylene, aromatic, amine and hydroxyl groups, respectively.

Figures

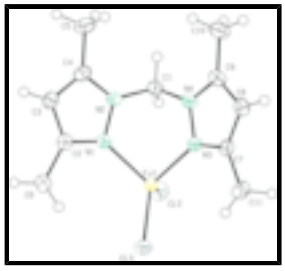

Fig. 1. Molecular structure and atomic numbering scheme showing 50% probability displacement ellipsoids in (I).

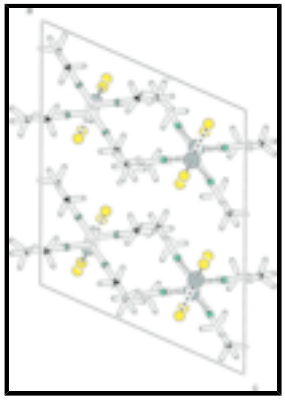

Fig. 2. Packing in the unit cell.

Dichlorido[(3,5-dimethyl-1*H*-pyrazol-1-yl)methane]copper(II)

Crystal data

$[CuCl_2(C_{11}H_{16}N_4)]$	F_{000} = 1384
M_r = 338.72	D_x = 1.585 Mg m^{-3}
Monoclinic, *C*2/*c*	Melting point: 471 K
Hall symbol: -C 2yc	Mo *K*α radiation λ = 0.71073 Å
a = 14.8120 (7) Å	Cell parameters from 2790 reflections
b = 16.7384 (9) Å	θ = 1.0–26.2º
c = 12.4943 (6) Å	μ = 1.90 mm^{-1}
β = 113.58 (1)º	*T* = 193 (2) K
V = 2839.0 (3) Å^3	Needle, green
Z = 8	0.2 × 0.1 × 0.1 mm

Data collection

Stoe IPDSII diffractometer	2790 independent reflections
Radiation source: fine-focus sealed tube	2619 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.431

Detector resolution: 150 pixels mm^{-1}

T = 193(2) K

ω scans

Absorption correction: none

39701 measured reflections

θ_{max} = 26.3º

θ_{min} = 1.9º

h = −18→16

k = 0→20

l = 0→15

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.030

$wR(F^2)$ = 0.075

S = 1.11

2790 reflections

167 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0335P)^2 + 8.2559P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max}$ = 0.49 e $Å^{-3}$

$\Delta\rho_{min}$ = −0.37 e $Å^{-3}$

Extinction correction: none

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.22280 (2)	0.382801 (16)	0.73912 (2)	0.01924 (10)
Cl2	0.38607 (4)	0.38971 (4)	0.81853 (6)	0.03166 (15)
Cl3	0.15000 (4)	0.50151 (3)	0.70045 (5)	0.02650 (14)
N4	0.18202 (15)	0.22504 (12)	0.81646 (18)	0.0246 (4)
N2	0.18482 (15)	0.22408 (12)	0.62680 (18)	0.0234 (4)
N1	0.17654 (15)	0.30433 (12)	0.60113 (18)	0.0239 (4)
N3	0.17098 (15)	0.30531 (12)	0.83008 (18)	0.0228 (4)
C1	0.23608 (18)	0.20058 (15)	0.7477 (2)	0.0243 (5)
H1A	0.3023	0.2253	0.7801	0.029*
H1B	0.2446	0.1418	0.7524	0.029*
C2	0.12575 (18)	0.30910 (15)	0.4853 (2)	0.0248 (5)
C9	0.13452 (18)	0.18129 (16)	0.8687 (2)	0.0272 (5)
C4	0.14092 (17)	0.17955 (15)	0.5294 (2)	0.0257 (5)
C10	0.1347 (2)	0.09174 (17)	0.8698 (3)	0.0378 (6)
H10A	0.1020	0.0718	0.7897	0.057*
H10B	0.0995	0.0726	0.9166	0.057*
H10C	0.2028	0.0723	0.9040	0.057*
C7	0.11546 (18)	0.31124 (15)	0.8915 (2)	0.0243 (5)
C3	0.10333 (18)	0.23234 (16)	0.4379 (2)	0.0265 (5)
H3	0.0687	0.2192	0.3578	0.032*
C8	0.09196 (19)	0.23490 (16)	0.9179 (2)	0.0285 (5)
H8	0.0539	0.2225	0.9615	0.034*
C5	0.1358 (2)	0.09069 (16)	0.5300 (3)	0.0354 (6)
H5A	0.2010	0.0690	0.5777	0.053*

H5B	0.1142	0.0706	0.4499	0.053*
H5C	0.0887	0.0740	0.5628	0.053*
C11	0.0867 (2)	0.39044 (16)	0.9220 (2)	0.0321 (6)
H11A	0.1174	0.4329	0.8941	0.048*
H11B	0.1089	0.3945	1.0070	0.048*
H11C	0.0149	0.3961	0.8851	0.048*
C6	0.1003 (2)	0.38793 (16)	0.4253 (2)	0.0323 (6)
H6A	0.1371	0.4302	0.4795	0.048*
H6B	0.0295	0.3976	0.3996	0.048*
H6C	0.1177	0.3878	0.3574	0.048*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01992 (16)	0.01714 (15)	0.01992 (15)	0.00007 (10)	0.00719 (11)	−0.00023 (10)
Cl2	0.0218 (3)	0.0354 (3)	0.0340 (3)	0.0002 (2)	0.0072 (2)	−0.0008 (3)
Cl3	0.0277 (3)	0.0202 (3)	0.0299 (3)	0.0015 (2)	0.0096 (2)	0.0004 (2)
N4	0.0268 (10)	0.0203 (10)	0.0275 (11)	0.0018 (8)	0.0118 (9)	0.0021 (8)
N2	0.0260 (10)	0.0191 (10)	0.0253 (10)	0.0023 (8)	0.0105 (8)	0.0002 (8)
N1	0.0276 (10)	0.0199 (10)	0.0243 (10)	0.0024 (8)	0.0106 (8)	0.0022 (8)
N3	0.0249 (10)	0.0185 (10)	0.0237 (10)	0.0014 (8)	0.0083 (8)	−0.0004 (8)
C1	0.0255 (12)	0.0225 (12)	0.0241 (12)	0.0038 (9)	0.0092 (10)	0.0019 (9)
C2	0.0231 (12)	0.0283 (13)	0.0230 (12)	0.0007 (10)	0.0093 (10)	0.0001 (10)
C9	0.0245 (12)	0.0260 (13)	0.0289 (12)	−0.0002 (10)	0.0085 (10)	0.0056 (10)
C4	0.0212 (11)	0.0249 (13)	0.0300 (13)	0.0001 (9)	0.0091 (10)	−0.0058 (10)
C10	0.0448 (17)	0.0252 (14)	0.0472 (17)	0.0000 (12)	0.0224 (14)	0.0067 (12)
C7	0.0245 (12)	0.0279 (13)	0.0195 (11)	0.0018 (10)	0.0076 (9)	−0.0011 (9)
C3	0.0249 (12)	0.0286 (13)	0.0241 (12)	−0.0027 (10)	0.0077 (10)	−0.0039 (10)
C8	0.0291 (13)	0.0322 (13)	0.0271 (13)	0.0005 (11)	0.0142 (11)	0.0024 (11)
C5	0.0365 (15)	0.0232 (13)	0.0400 (15)	0.0031 (11)	0.0082 (12)	−0.0056 (11)
C11	0.0354 (14)	0.0339 (14)	0.0314 (14)	0.0034 (11)	0.0181 (12)	−0.0033 (11)
C6	0.0407 (15)	0.0287 (14)	0.0278 (13)	0.0020 (11)	0.0139 (12)	0.0034 (11)

Geometric parameters (Å, °)

Cu1—N1	2.055 (2)	C4—C3	1.374 (4)
Cu1—N3	2.064 (2)	C4—C5	1.490 (4)
Cu1—Cl2	2.2195 (9)	C10—H10A	0.9800
Cu1—Cl3	2.2197 (7)	C10—H10B	0.9800
N4—C9	1.351 (3)	C10—H10C	0.9800
N4—N3	1.372 (3)	C7—C8	1.398 (4)
N4—C1	1.448 (3)	C7—C11	1.488 (4)
N2—C4	1.352 (3)	C3—H3	0.9500
N2—N1	1.375 (3)	C8—H8	0.9500
N2—C1	1.448 (3)	C5—H5A	0.9800
N1—C2	1.340 (3)	C5—H5B	0.9800
N3—C7	1.334 (3)	C5—H5C	0.9800
C1—H1A	0.9900	C11—H11A	0.9800
C1—H1B	0.9900	C11—H11B	0.9800

C2—C3	1.398 (4)	C11—H11C	0.9800
C2—C6	1.490 (4)	C6—H6A	0.9800
C9—C8	1.375 (4)	C6—H6B	0.9800
C9—C10	1.499 (4)	C6—H6C	0.9800
N1—Cu1—N3	89.30 (8)	C9—C10—H10A	109.5
N1—Cu1—Cl2	110.26 (7)	C9—C10—H10B	109.5
N3—Cu1—Cl2	111.42 (6)	H10A—C10—H10B	109.5
N1—Cu1—Cl3	114.82 (6)	C9—C10—H10C	109.5
N3—Cu1—Cl3	115.28 (6)	H10A—C10—H10C	109.5
Cl2—Cu1—Cl3	113.46 (3)	H10B—C10—H10C	109.5
C9—N4—N3	111.1 (2)	N3—C7—C8	109.7 (2)
C9—N4—C1	130.7 (2)	N3—C7—C11	121.3 (2)
N3—N4—C1	118.2 (2)	C8—C7—C11	129.0 (2)
C4—N2—N1	111.3 (2)	C4—C3—C2	106.9 (2)
C4—N2—C1	130.7 (2)	C4—C3—H3	126.6
N1—N2—C1	118.00 (19)	C2—C3—H3	126.6
C2—N1—N2	105.6 (2)	C9—C8—C7	106.8 (2)
C2—N1—Cu1	136.29 (17)	C9—C8—H8	126.6
N2—N1—Cu1	117.39 (15)	C7—C8—H8	126.6
C7—N3—N4	106.0 (2)	C4—C5—H5A	109.5
C7—N3—Cu1	136.09 (17)	C4—C5—H5B	109.5
N4—N3—Cu1	117.25 (15)	H5A—C5—H5B	109.5
N2—C1—N4	111.01 (19)	C4—C5—H5C	109.5
N2—C1—H1A	109.4	H5A—C5—H5C	109.5
N4—C1—H1A	109.4	H5B—C5—H5C	109.5
N2—C1—H1B	109.4	C7—C11—H11A	109.5
N4—C1—H1B	109.4	C7—C11—H11B	109.5
H1A—C1—H1B	108.0	H11A—C11—H11B	109.5
N1—C2—C3	109.8 (2)	C7—C11—H11C	109.5
N1—C2—C6	121.1 (2)	H11A—C11—H11C	109.5
C3—C2—C6	129.2 (2)	H11B—C11—H11C	109.5
N4—C9—C8	106.4 (2)	C2—C6—H6A	109.5
N4—C9—C10	123.2 (2)	C2—C6—H6B	109.5
C8—C9—C10	130.4 (2)	H6A—C6—H6B	109.5
N2—C4—C3	106.5 (2)	C2—C6—H6C	109.5
N2—C4—C5	123.6 (2)	H6A—C6—H6C	109.5
C3—C4—C5	129.9 (2)	H6B—C6—H6C	109.5

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1B···Cl3^{i}	0.99	2.75	3.674 (2)	155
C6—H6C···Cl3^{ii}	0.98	2.87	3.676 (3)	140
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Symmetry codes: (i) −*x*+1/2, *y*−1/2, −*z*+3/2; (ii) *x*, −*y*+1, *z*−1/2; (iii) *x*, −*y*+1, *z*+1/2; (iv) −*x*, *y*, −*z*+3/2.

Fig. 1

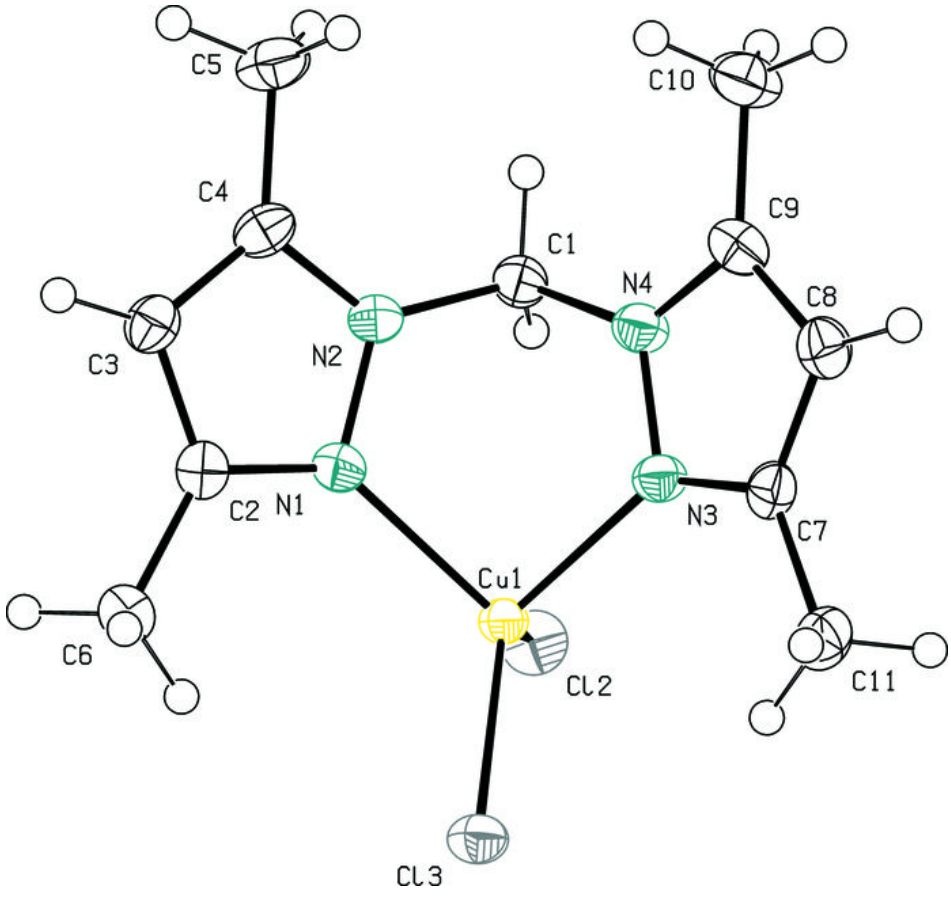

Fig. 2