Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Chlorido(11-methyldipyrido[3,2-*a*:-2′,3′-*c*]phenazine-κ^2N^4,N^5)copper(I)

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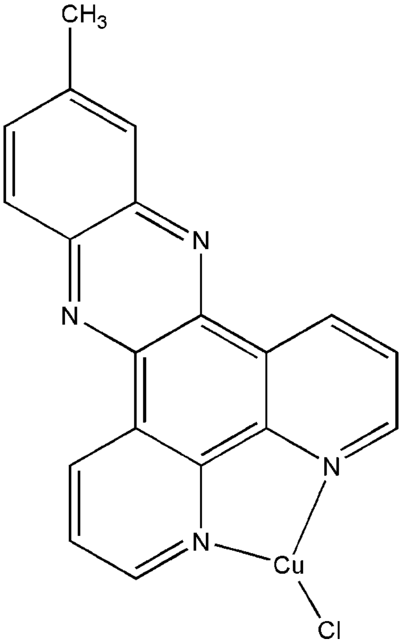
Received 12 July 2007; accepted 24 July 2007

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.008 Å; disorder in main residue; R factor = 0.057; wR factor = 0.203; data-to-parameter ratio = 13.3.

In the title compound, $[CuCl(C_{19}H_{11}N_4)]$, the Cu^I ion is coordinated by one Cl^- ion and two N atoms from a chelating 11-methyldipyrido[3,2-*a*:2′,3′-*c*]phenazine ligand. The Cu^I and Cl^- ions are situated on a mirror plane and the terminal methyl group of the ligand is disordered equally over two positions. Aromatic π–π stacking interactions [centroid separations = 3.609 (3)–3.669 (3) Å] help to stabilize the crystal packing.

Related literature

For related structures, see: Li, Dong *et al.* (2006); Li, Fang *et al.* (2006). For background, see: Lu (2003); Cheng *et al.* (2004); Chen & Liu (2002). For the ligand synthesis, see: Steck & Day (1943).



Experimental

Crystal data

$[CuCl(C_{19}H_{11}N_4)]$
M_r = 394.31
Orthorhombic, *Pnma*
a = 25.947 (4) Å
b = 12.1604 (17) Å
c = 4.9456 (7) Å
V = 1560.5 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.58 mm^{-1}
T = 293 (2) K
0.49 × 0.11 × 0.05 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.812, T_{max} = 0.924
7882 measured reflections
1615 independent reflections
822 reflections with $I > 2\sigma(I)$
R_{int} = 0.066

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.203
S = 1.02
1615 reflections
121 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.50 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	2.054 (5)	Cu1—Cl1	2.105 (2)
$N1^i$—Cu1—N1	81.5 (3)	N1—Cu1—Cl1	139.24 (13)

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

This work was supported by the Natural Science Foundation of Jilin Province (grant No. 2005103).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2482).

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doi:10.1107/S1600536807036173

supplementary materials

Acta Cryst. (2007). E**63**, m2229 [**doi:10.1107/S1600536807036173**]

Chlorido(11-methyldipyrido[3,2-*a*:2',3'-*c*]phenazine-κ^2N^4,N^5)copper(I)

C.-B. Li, **S. Zhou**, **G.-G. Gao** and **B. Liu**

Comment

Recently, the construction of supramolecular architectures has attracted much attention for their intriguing structural features (Lu, 2003; Cheng *et al.*, 2004). The 1,10-phenanthroline ligand has been widely used for the synthesis of coordination complexes; these are sometimes assembled into supramolecular architectures through aromatic π-π interactions (Chen & Liu, 2002). Dipyrido[3,2 − a:2',3'-c]phenazine is a similarly useful ligand, and several complexes have been reported (Li, Fang, Gao *et al.*, 2006). To extend our recent work, we obtained the title compound, (I), by using 11-methyldipyrido[3,2 − a:2',3'-c]phenazine (MDPPz), 1,3-benzene dicarboxylic acid (which was not incorporated into the product) and $CuCl_2$ as starting materials. The starting Cu^{II} was reduced to Cu^I by an unknown process.

In complex (I), the Cu^I ion is coordinated by two N atoms belonging to the bidentate MDPPz ligand and one Cl^- ion, resulting in a CuN_2Cl triangular geometry (Table 1, Fig. 1). The Cu^I and Cl^- ions are situated on a mirror plane which also perpendicularly passes through the MSPPz ligand, thus the methyl group belonging to the MSPPz ligand is disordered and its occupancy is assigned as 0.5. There are π-π stacking interactions between the neighboring parallel MSDPPz liands, which the nearer centroid-to-centroid distance of aromatic rings is in the range 3.609 (3)—3.669 (3)Å (Fig. 2). These weak interactions consolidate the packing of (I).

Experimental

The MDPPz ligand was synthesized by the literature method of Steck & Day (1943). A mixture of $CuCl_2$ (0.3 mmol), MDPPz (0.3 mmol) and 1,3-benzene dicarboxylic acid (0.6 mmol) in distilled water (30 ml) was stirred thoroughly for 1 h at ambient temperature. The pH was adjusted to about 5 with aqueous NaOH solution. The suspension was then sealed in a Teflon-lined stainless steel reaction vessel (40 ml) and heated at 443 K for 4 d. The vessel was then cooled slowly to room temperature at a rate of 5 K /h before opening, and reddish brown crystals of (I) were collected.

Refinement

The positional parameters of the H atoms were calculated geometrically (C—H = 0.93–0.96 Å) and refined as riding with $U_{iso} = 1.2U_{eq}(C)$ or $1.5U_{eq}$(methyl C).

Figures

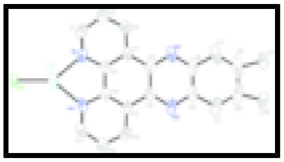

Fig. 1. The molecular structure of (I). Displacement ellipsoids are drawn at 30% probability level (H atoms are omitted for clarity) [Symmetry code: i) x, $1/2 - y$, z.].

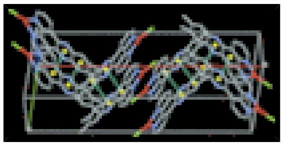

Fig. 2. The packing diagram of (I) (H atoms were omitted for clarity; the centroid-to-centroid distances are shown as dashed line.).

Chlorido(11-methyldipyrido[3,2 – a:2',3'-c]phenazine-κ^2N^4,N^5)copper(I)

Crystal data

$[CuCl(C_{19}H_{11}N_4)]$

$M_r = 394.31$

Orthorhombic, *Pnma*

$a = 25.947$ (4) Å

$b = 12.1604$ (17) Å

$c = 4.9456$ (7) Å

$V = 1560.5$ (4) Å^3

$Z = 4$

$F_{000} = 796$

$D_x = 1.678$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Cell parameters from 2310 reflections

$\theta = 2.1$–25.3°

$\mu = 1.58$ mm^{-1}

$T = 293$ (2) K

Block, reddish brown

0.49 × 0.11 × 0.05 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293(2)$ K

ω scans

Absorption correction: multi-scan (SADABS; Bruker, 2002)

$T_{min} = 0.812$, $T_{max} = 0.924$

7882 measured reflections

1615 independent reflections

822 reflections with $I > 2\sigma(I)$

$R_{int} = 0.066$

$\theta_{max} = 26.1$°

$\theta_{min} = 2.3$°

$h = -16 \rightarrow 32$

$k = -14 \rightarrow 15$

$l = -5 \rightarrow 6$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.057$

$wR(F^2) = 0.203$

$S = 1.02$

1615 reflections

121 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

$w = 1/[\sigma^2(F_o^2) + (0.1074P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.50$ e Å^{-3}

$\Delta\rho_{min} = -0.45$ e Å^{-3}

Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$	Occ. (<1)
Cu1	0.98473 (4)	0.2500	0.1790 (2)	0.1045 (6)	
Cl1	1.04420 (8)	0.2500	−0.1105 (4)	0.0798 (7)	
N2	0.81629 (16)	0.1340 (4)	1.1113 (8)	0.0742 (13)	
N1	0.94108 (15)	0.1397 (4)	0.3947 (8)	0.0660 (12)	
C5	0.84651 (18)	0.1914 (4)	0.9473 (9)	0.0625 (13)	
C8	0.7193 (2)	0.1927 (7)	1.6198 (11)	0.124 (4)	
C4	0.87997 (17)	0.1316 (5)	0.7633 (10)	0.0606 (13)	
C9	0.91021 (18)	0.1903 (4)	0.5804 (9)	0.0596 (13)	
C1	0.9417 (2)	0.0309 (6)	0.3921 (12)	0.0786 (16)	
H1A	0.9617	−0.0041	0.2621	0.094*	
C2	0.9142 (2)	−0.0339 (5)	0.5726 (13)	0.0851 (17)	
H2A	0.9168	−0.1102	0.5677	0.102*	
C3	0.8830 (2)	0.0173 (5)	0.7586 (13)	0.0772 (16)	
H3A	0.8641	−0.0242	0.8811	0.093*	
C7	0.7512 (2)	0.1350 (7)	1.4547 (12)	0.103 (2)	
H7A	0.7505	0.0585	1.4568	0.124*	
C6	0.7858 (2)	0.1912 (5)	1.2780 (10)	0.0812 (19)	
C10	0.6809 (4)	0.1629 (11)	1.814 (2)	0.089 (4)	0.50
H10A	0.6669	0.2282	1.8944	0.133*	0.50
H10B	0.6962	0.1179	1.9518	0.133*	0.50
H10C	0.6539	0.1226	1.7259	0.133*	0.50

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0553 (7)	0.1961 (15)	0.0621 (8)	0.000	0.0113 (5)	0.000
Cl1	0.0772 (14)	0.0847 (14)	0.0774 (12)	0.000	0.0374 (10)	0.000
N2	0.046 (3)	0.126 (4)	0.051 (2)	−0.010 (2)	−0.002 (2)	0.012 (2)
N1	0.050 (3)	0.096 (4)	0.052 (2)	0.009 (2)	−0.0027 (19)	−0.009 (2)
C5	0.044 (3)	0.100 (4)	0.043 (2)	−0.005 (2)	−0.008 (2)	0.004 (2)
C8	0.047 (3)	0.274 (12)	0.051 (3)	−0.013 (4)	−0.002 (3)	0.019 (4)
C4	0.041 (3)	0.087 (4)	0.053 (3)	−0.004 (3)	−0.002 (2)	0.002 (3)

C9	0.045 (3)	0.086 (3)	0.047 (3)	0.001 (2)	−0.008 (2)	−0.002 (2)
C1	0.059 (4)	0.101 (5)	0.076 (4)	0.015 (3)	−0.005 (3)	−0.020 (4)
C2	0.075 (4)	0.096 (4)	0.085 (4)	0.004 (3)	0.002 (3)	−0.004 (4)
C3	0.070 (4)	0.091 (4)	0.070 (3)	−0.003 (3)	−0.001 (3)	0.011 (3)
C7	0.054 (4)	0.192 (7)	0.063 (4)	−0.016 (4)	0.000 (3)	0.025 (4)
C6	0.043 (3)	0.157 (6)	0.043 (3)	−0.007 (3)	0.000 (2)	0.008 (3)
C10	0.061 (7)	0.133 (10)	0.072 (8)	−0.022 (7)	0.011 (6)	0.008 (7)

Geometric parameters (Å, °)

Cu1—N1$^{\mathrm{i}}$	2.054 (5)	C4—C9	1.394 (6)
Cu1—N1	2.054 (5)	C9—C9$^{\mathrm{i}}$	1.453 (10)
Cu1—Cl1	2.105 (2)	C1—C2	1.389 (8)
N2—C5	1.326 (6)	C1—H1A	0.9300
N2—C6	1.337 (7)	C2—C3	1.374 (8)
N1—C1	1.323 (7)	C2—H2A	0.9300
N1—C9	1.365 (6)	C3—H3A	0.9300
C5—C5$^{\mathrm{i}}$	1.425 (10)	C7—C6	1.428 (8)
C5—C4	1.453 (7)	C7—H7A	0.9300
C8—C7	1.358 (9)	C6—C6$^{\mathrm{i}}$	1.429 (12)
C8—C8$^{\mathrm{i}}$	1.395 (17)	C10—H10A	0.9600
C8—C10	1.430 (11)	C10—H10B	0.9600
C4—C3	1.392 (7)	C10—H10C	0.9600
N1$^{\mathrm{i}}$—Cu1—N1	81.5 (3)	N1—C1—H1A	118.1
N1$^{\mathrm{i}}$—Cu1—Cl1	139.24 (13)	C2—C1—H1A	118.1
N1—Cu1—Cl1	139.24 (13)	C3—C2—C1	118.4 (6)
C5—N2—C6	116.9 (5)	C3—C2—H2A	120.8
C1—N1—C9	117.6 (5)	C1—C2—H2A	120.8
C1—N1—Cu1	129.9 (4)	C2—C3—C4	119.8 (6)
C9—N1—Cu1	112.3 (4)	C2—C3—H3A	120.1
N2—C5—C5$^{\mathrm{i}}$	121.7 (3)	C4—C3—H3A	120.1
N2—C5—C4	118.2 (5)	C8—C7—C6	120.3 (8)
C5$^{\mathrm{i}}$—C5—C4	120.0 (3)	C8—C7—H7A	119.9
C7—C8—C8$^{\mathrm{i}}$	121.1 (5)	C6—C7—H7A	119.9
C7—C8—C10	134.3 (9)	N2—C6—C7	120.0 (6)
C8$^{\mathrm{i}}$—C8—C10	104.6 (6)	N2—C6—C6$^{\mathrm{i}}$	121.3 (3)
C3—C4—C9	117.9 (5)	C7—C6—C6$^{\mathrm{i}}$	118.6 (4)
C3—C4—C5	123.0 (5)	C8—C10—H10A	109.5
C9—C4—C5	119.1 (5)	C8—C10—H10B	109.5
N1—C9—C4	122.4 (5)	H10A—C10—H10B	109.5
N1—C9—C9$^{\mathrm{i}}$	116.8 (3)	C8—C10—H10C	109.5
C4—C9—C9$^{\mathrm{i}}$	120.8 (3)	H10A—C10—H10C	109.5
N1—C1—C2	123.7 (6)	H10B—C10—H10C	109.5

Symmetry codes: (i) x, $-y+1/2$, z.

Fig. 1

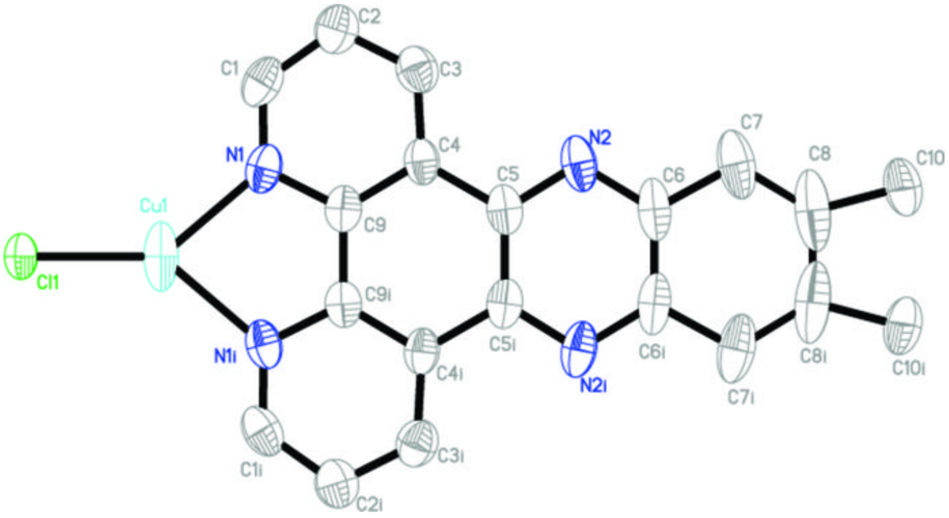
C2
C1
C3
N1
C4
N2
C5
C6
C7
C8
C10
Cu1
C9
Cl1
C9i
N1i
C4i
C5i
N2i
C6i
C7i
C8i
C10i
C1i
C3i
C2i

Fig. 2