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Bis(2,2′-bipyridine-κ^2N,N')chlorocopper(II) tetrafluoroborate dichloromethane solvate

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The new mononuclear copper(II) complex, $[CuCl(C_{10}H_8N_2)_2]BF_4 \cdot CH_2Cl_2$, was prepared by a new procedure using photo-irradiation and a nitrogen atmosphere. X-ray analysis reveals a slightly distorted trigonal–bipyramidal coordination geometry of copper(II); the axial ligands and the Cu^{II} atom deviate slightly from linearity [N—Cu—N = 175.3 (3)°].

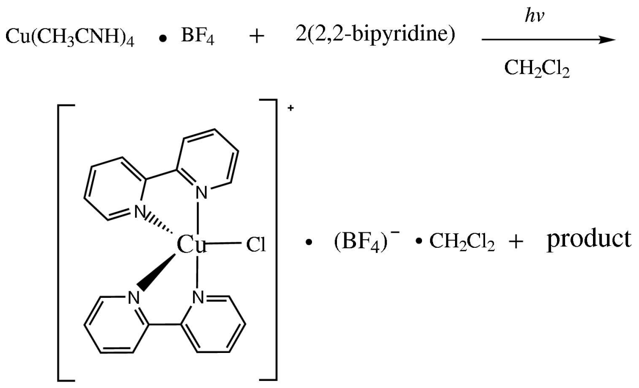
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.012 Å
Disorder in solvent or counterion
R factor = 0.074
wR factor = 0.223
Data-to-parameter ratio = 11.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The copper(I) complex of $[Cu(dmp)_2]^+$ (dmp = 2,9-dimethyl-1,10-phenanthroline) can be photo-oxidized to $[Cu(dmp)_2]^{2+}$ when irradiated by high-energy laser light in CH_2Cl_2 solution (Horváth & Stevenson, 1993). The same procedure was used to obtain the copper(II) complex $[Cu(bipy)_2Cl]BF_4$ (bipy is 2,2′-bipyridine) (see scheme). The copper(II) complex $[Cu(bipy)_2Cl]BF_4$ has already been prepared by a different procedure (Nagle *et al.*, 1990); the complex was obtained using a copper(II) ion in an alcohol–water reaction system. In the complex obtained by Nagle *et al.* (1990), the Cu^{II} atom is coordinated by two 2,2′-bipyridyl ligands and by one Cl atom and exhibits a distorted geometry between square-based pyramidal and trigonal–bipyramidal.



(I)

In the title complex, (I), the Cu^{II} atom is also coordinated by two 2,2′-bipyridyl ligands and one Cl atom in a slightly distorted trigonal–bipyramidal geometry (Fig. 1). The axial bond distances Cu—N1 and Cu—N3 are 1.995 (6) and 1.986 (5) Å, respectively (mean 1.991 Å). The equatorial bond distances Cu—N2 and Cu—N4 are 2.104 (6) and 2.100 (5) Å, respectively (mean 2.102 Å). The Cu—N distances in (I) (Table 1) are comparable with those in related compounds (Murphy, Nagle *et al.*, 1997; Murphy, Murphy *et al.*, 1997; O'Sullivan *et al.*, 1999; Ma *et al.*, 1999); differences between the title compound and the literature data are within standard deviations of chemically analogous bonds. However, differ-

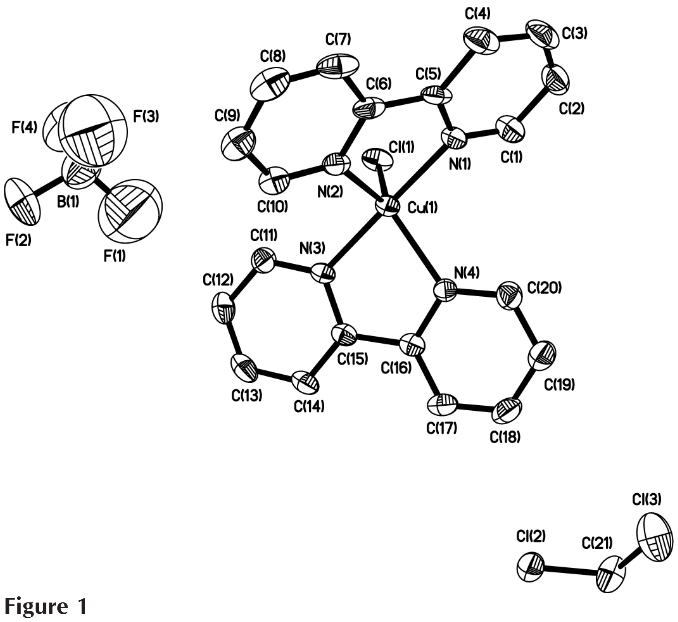


Figure 1
View of (I), shown with 30% probability displacement ellipsoids. H atoms have been omitted for clarity. Only one disorder component is shown.

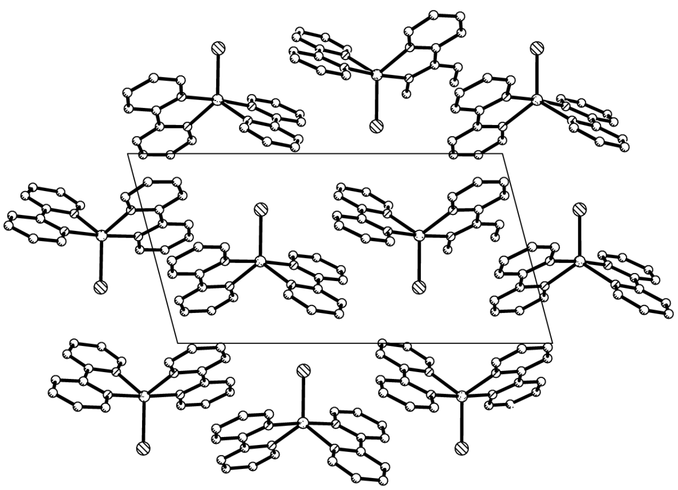


Figure 2
The packing of (I), viewed along the *b* axis. H atoms have been omitted for clarity. Only one disorder component is shown.

ences in molecular geometries between the complex reported by Nagle *et al.* (1990) and the title compound are significant; the two bonds Cu—N1 and Cu—N3 in (I) differ by 0.009 Å, whereas the analogous bonds reported by Nagle *et al.* differ by 0.023 Å. The difference between the two bond lengths Cu—N2 and Cu—N4 is 0.063 Å (Nagle *et al.*, 1990), whereas in the title compound, the difference (0.004 Å) is less than a standard deviation (0.006 Å). The Cu—Cl bond distance is 2.333 Å in (I), which is longer than the Cu—Cl bond distance (2.285 Å) reported by Nagle *et al.* (1990). Differences in bond angles between these two structures are even more pronounced; the trigonal–bipyramidal coordination geometry of (I) reveals nearly linear axial bonds [N1—Cu—N3 = 175.3 (3)°] and the mean value of the bond angles for equatorial ligands (with Cu^{II} as the central atom) is 120.0°. As the coordination of the complex reported by Nagle *et al.* (1990) represents a transition between square-pyramidal and trigonal–bipyramidal, the bond angles deviate significantly from the usual values for the two ideal geometries. In the crystal structure, a BF_4^- anion is disordered over two orientations with approximately equal populations; a dichloromethane solvent molecule is disordered over two positions with approximately equal populations. The packing of (I) is shown in Fig. 2.

Experimental

For the synthesis of (I), a mixture of $[Cu(MeCN)_4]BF_4$ (100.0 mg, 0.317 mmol) and 2,2′-bipyridine (99.2 mg, 0.634 mmol) in dichloromethane (25 ml) was stirred for 4 h at room temperature under photoirradiation (365 nm). Green crystals suitable for X-ray diffraction analysis were obtained by recrystallization of the crude product from a dichloromethane–diethyl ether solution. The compound was obtained in 62% yield and identified as $[CuCl(2,2'\text{-bipyridine})_2]BF_4.CH_2Cl_2$. Elemental analysis calculated (%) for $C_{21}H_{18}BCl_3CuF_4N_4$: C43.22, H 3.09, N 9.60, found (%): C 43.27, H 3.10, N 9.55.

Crystal data

$[CuCl(C_{10}H_8N_2)_2]BF_4{\cdot}CH_2Cl_2$
$M_r = 583.09$
Monoclinic, $P2_1/c$
$a = 7.491$ (3) Å
$b = 23.458$ (8) Å
$c = 14.302$ (5) Å
$\beta = 104.803$ (6)°
$V = 2429.7$ (14) Å^3
$Z = 4$
$D_x = 1.594$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 820 reflections
$\theta = 2.9$–25.7°
$\mu = 1.28$ mm^{-1}
$T = 293$ (2) K
Block, green
0.22 × 0.20 × 0.18 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.691$, $T_{max} = 0.795$
12 474 measured reflections
4267 independent reflections
2452 reflections with $I > 2\sigma(I)$
$R_{int} = 0.061$
$\theta_{max} = 25.0°$
$h = -8 \rightarrow 8$
$k = -12 \rightarrow 27$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.074$
$wR(F^2) = 0.223$
$S = 1.02$
4267 reflections
372 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1219P)^2 + 1.687P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 1.00$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N3	1.986 (5)	Cu1—N2	2.104 (6)
Cu1—N1	1.995 (6)	Cu1—Cl1	2.333 (2)
Cu1—N4	2.100 (5)		
N3—Cu1—N1	175.3 (3)	N4—Cu1—N2	118.5 (2)
N3—Cu1—N4	80.3 (2)	N3—Cu1—Cl1	92.10 (18)
N1—Cu1—N4	98.2 (2)	N1—Cu1—Cl1	92.44 (19)
N3—Cu1—N2	97.1 (2)	N4—Cu1—Cl1	121.16 (16)
N1—Cu1—N2	79.7 (2)	N2—Cu1—Cl1	120.30 (16)

All H atoms were initially located in a difference Fourier map. Aromatic H atoms were placed in geometrically idealized positions and constrained to C—H distances of 0.93 Å and U_{iso}(H) values of

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$1.5U_{eq}$(C). The H atoms of the dichloromethane solvent were constrained to an ideal geometry, with C—H distances of 0.96 Å and U_{iso}(H) values of $1.5U_{eq}$(C) and refined as riding.

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

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