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Key indicators

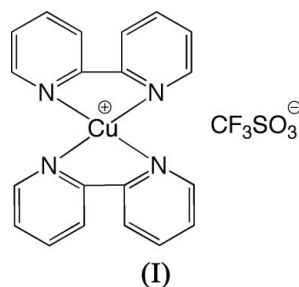
Single-crystal X-ray study
 $T = 273$ K
Mean $\sigma(\text{C}-\text{C}) = 0.006$ Å
 R factor = 0.036
 wR factor = 0.126
Data-to-parameter ratio = 17.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Bis(2,2'-bipyridine- κ^2N,N')copper(I)
trifluoromethanesulfonate

In the title compound, $[\text{Cu}(\text{C}_{10}\text{H}_8\text{N}_2)_2](\text{CF}_3\text{O}_3\text{S})$, the Cu^{I} ion is chelated by two 2,2'-bipyridine (bpy) ligands in a distorted tetrahedral coordination geometry. The average $\text{Cu}-\text{N}$ bond length is 2.024 (3) Å. The interligand dihedral angle is 87.5 (11)°. Weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonding between the Cu^{I} complex cation and the trifluoromethanesulfonate anion stabilizes the crystal structure.

Received 27 January 2006
Accepted 20 February 2006

Comment

The $[\text{Cu}^{\text{I}}(\text{bpy})_2][\text{Y}]$ compounds (where bpy = 2,2'-bipyridine; $\text{Y} = \text{Br}^-$, Cl^- , PF_6^- , ClO_4^- , BF_4^- etc.) are very active catalysts in atom transfer radical polymerization (ATRP) (Matyjaszewski & Xia, 2001; Kamigaito *et al.*, 2001; Wang & Matyjaszewski, 1995) and have been studied extensively utilizing a variety of spectroscopic techniques (Pintauer & Matyjaszewski, 2005; Pintauer *et al.*, 2003, 2000). The $[\text{Cu}^{\text{I}}(\text{bpy})_2][\text{Y}]$ compounds are typically prepared by mixing $\text{Cu}^{\text{I}}\text{Y}$ or $[\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_4][\text{Y}]$ with two equivalents of the ligand (Pintauer & Matyjaszewski, 2005). So far, structurally characterized $\text{Cu}^{\text{I}}(\text{bpy})_2$ complexes include $[\text{Cu}^{\text{I}}(\text{bpy})_2][\text{ClO}_4]$ (Munakata *et al.*, 1987), $[\text{Cu}^{\text{I}}(\text{bpy})_2][\text{PF}_6]$ (Foley *et al.*, 1984) and $[\text{Cu}^{\text{I}}(\text{bpy})_2][\text{Cu}^{\text{I}}\text{Cl}_2]$ (Skelton *et al.*, 1991). We have successfully isolated the title compound, (I), which is the fourth member of this family.



The crystal structure of (I) consists of Cu^{I} complex cations and trifluoromethanesulfonate anions (Fig. 1). The Cu^{I} ion is coordinated by four N atoms from two bpy ligands in a distorted tetrahedral coordination geometry (Table 1). The average $\text{Cu}-\text{N}$ bond length of 2.024 (3) Å is in agreement with those in previously characterized $[\text{Cu}^{\text{I}}(\text{bpy})_2]^+$ cations. The 'bite' angles in (I) are smaller than 90°, which is due to the rigid geometry of the bidentate bpy ligand.

The dihedral angle between two chelating bpy ligands usually affects the redox potential of the $[\text{Cu}^{\text{I}}(\text{bpy})_2]^+$ cation and consequently the stability constants of $[\text{Cu}^{\text{I}}(\text{bpy})_2]^+$ and $[\text{Cu}^{\text{II}}(\text{bpy})_2]^{2+}$ cations. The interligand dihedral angle of 87.5 (11)° in (I) is much higher than those found in

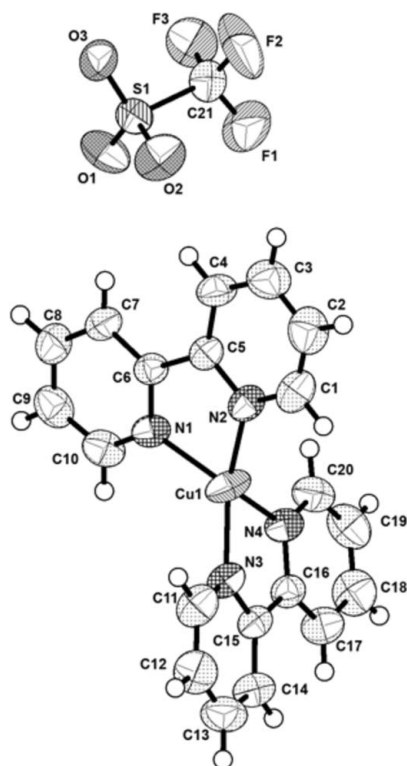


Figure 1
The asymmetric unit of (I) with 30% probability displacement ellipsoids (arbitrary spheres for H atoms).

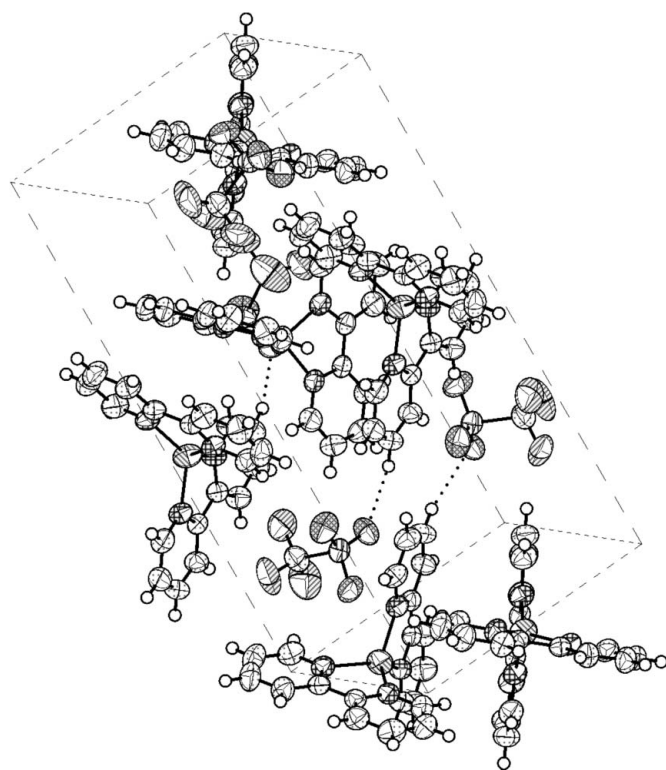


Figure 2
A packing diagram of (I), showing the weak C—H...O interaction (dotted lines).

$[\text{Cu}^{\text{I}}(\text{bpy})_2]^+$ cited above, *viz.* $[\text{Cu}^{\text{I}}(\text{bpy})_2][\text{ClO}_4]$ (75.2°), $[\text{Cu}^{\text{I}}(\text{bpy})_2][\text{PF}_6]$ (44.6°) and $[\text{Cu}^{\text{I}}(\text{bpy})_2][\text{Cu}^{\text{I}}\text{Cl}_2]$ (76.2°).

Weak C—H...O hydrogen bonding occurs between the Cu^{I} complex cation and trifluoromethanesulfonate anion (Table 2 and Fig. 2), which stabilizes the crystal structure of (I).

Experimental

Dry and degassed dichloromethane (10 ml) was added, under argon, to a Schlenk flask containing $[\text{Cu}^{\text{I}}(\text{CF}_3\text{SO}_3)_2] \cdot \text{C}_6\text{H}_5\text{CH}_3$ (0.100 g, 0.193 mmol) and 2,2'-bipyridine (0.0604 g, 0.387 mmol). The reaction mixture was stirred at room temperature for 30 min and the solvent was evaporated under vacuum. The product was washed with 2×10 ml of pentane and dried under vacuum to yield 0.176 g (87%) of (I). Crystals suitable for X-ray analysis were obtained by slow evaporation of a methanol solution at room temperature.

Crystal data

$[\text{Cu}(\text{C}_{10}\text{H}_8\text{N}_2)_2](\text{CF}_3\text{O}_3\text{S})$
 $M_r = 524.98$
 Orthorhombic, $P2_12_12_1$
 $a = 9.3749$ (4) Å
 $b = 11.6692$ (5) Å
 $c = 20.0628$ (9) Å
 $V = 2194.82$ (17) Å³
 $Z = 4$
 $D_x = 1.589$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 4628 reflections
 $\theta = 2.4\text{--}21.1^\circ$
 $\mu = 1.15$ mm⁻¹
 $T = 273$ (2) K
 Needle, red
 $0.30 \times 0.15 \times 0.07$ mm

Data collection

Bruker SMART APEX-II diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2002)
 $T_{\text{min}} = 0.810$, $T_{\text{max}} = 0.920$
 22333 measured reflections

5247 independent reflections
 3736 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.039$
 $\theta_{\text{max}} = 27.9^\circ$
 $h = -12 \rightarrow 12$
 $k = -15 \rightarrow 15$
 $l = -26 \rightarrow 26$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.126$
 $S = 0.81$
 5247 reflections
 298 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.25$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.24$ e Å⁻³
 Absolute structure: Flack (1983),
 2274 Friedel Pairs
 Flack parameter: 0.003 (15)

Table 1

Selected geometric parameters (Å, °).

Cu1—N1	2.034 (3)	Cu1—N3	2.004 (3)
Cu1—N2	2.005 (3)	Cu1—N4	2.046 (3)
N3—Cu1—N2	131.04 (11)	N3—Cu1—N4	81.56 (11)
N3—Cu1—N1	127.34 (12)	N2—Cu1—N4	126.56 (12)
N2—Cu1—N1	81.45 (10)	N1—Cu1—N4	113.67 (11)

Table 2

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
C2—H2...O2 ⁱ	0.93	2.45	3.359 (5)	165
C8—H7...O3 ⁱⁱ	0.93	2.57	3.478 (5)	166

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

H atoms were positioned geometrically (C–H = 0.93 Å) and treated with a riding model in subsequent refinement cycles. The isotropic displacement parameters were set to $1.2U_{\text{eq}}$ of the carrier atom.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1998); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL*.

Financial support from Duquesne University (Start-up Grant) is greatly acknowledged.

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