Supramolecular interactions in a copper(II) 4′-(4-bromophenyl)-2,2′:6′,2″-terpyridine complex

Ludwig Chenneberg, Janaina G. Ferreira* and Garry S. Hanan

Département de Chimie, Université de Montréal, CP 6128, Succ. Centre-ville, Montréal, Québec, Canada H3C 3J7

Correspondence e-mail: j.gomes.ferreira@umontreal.ca

The title compound, [4′-(4-bromophenyl)-2,2′:6′,2″-terpyridine]chlorido(trifluoromethanesulfonato)copper(II), [Cu(CF$_3$O$_3$S)Cl(C$_{21}$H$_{14}$BrN$_3$)], is a new copper complex containing a polypyridyl-based ligand. The Cu^{II} centre is five-coordinated in a square-pyramidal manner by one substituted 2,2′:6′,2″-terpyridine ligand, one chloride ligand and a coordinated trifluoromethanesulfonate anion. The Cu—N bond lengths differ by 0.1 Å for the peripheral and central pyridine rings [2.032 (2) (mean) and 1.9345 (15) Å, respectively]. The presence of the trifluoromethanesulfonate anion coordinated to the metal centre allows Br···F halogen–halogen interactions, giving rise to the formation of a dimer about an inversion centre. This work also demonstrates that the rigidity of the ligand allows the formation of other types of nonclassical interactions (C—H···Cl and C—H···O), yielding a three-dimensional network.

Comment

Polypyridine ligands, e.g. 2,2′:6′,2″-terpyridine (tpy), have been the focus of much attention due to their incorporation into devices with many potential applications, such as electrochromic materials, anion-recognition devices and solar photovoltaic cells (Han et al., 2008; Bhaumik et al., 2010). In particular, several ruthenium(II) complexes based on polypyridine ligands have been prepared and structurally characterized. Heteroleptic complexes are designed to increase the excited-state lifetime of ruthenium(II) bis(tpy) complexes for use in such devices (Rajeshwar et al., 2008). In the literature there are, however, fewer examples of Cu^{II} complexes of substituted tpy ligands and their derivatives (Chen et al., 2010; McMurtrie & Dance, 2009; Uma et al., 2005; Medlycott et al., 2008; Wang et al., 2009). Previous work by our group has described the synthesis of new homoleptic tridentate complexes containing one central triazine ring that may be applied to the development of new redox mediators (Medly-

cott et al., 2007, 2008). As an extension of this study, we are currently investigating the supramolecular reactivity of the tridentate pyridyl-substituted ligand tpy to form copper complexes. Against this background, we present here the structure of the title copper–tpy complex, (I).

(I)
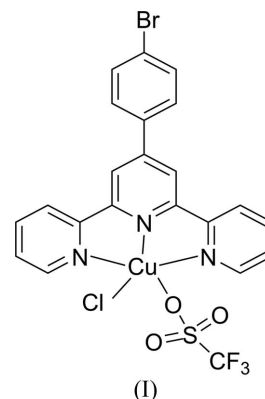
The Cu^{II} centre in (I) is coordinated in a slightly distorted square-pyramidal environment by three N-atom donors from the tridentate ligand. The Cl atom occupies the fourth coordination site of the basal plane, with an O atom of the trifluoromethanesulfonate (triflate) ligand occupying the apical position. The three N atoms and Cl atom of the basal plane are nearly coplanar, with the largest deviation from the least-squares plane being 0.0524 (8) Å for atom N2. The Cu atom is displaced by 0.1420 (7) Å out of the basal plane.

The Cu—N and Cu—Cl distances (Table 1) are comparable with those found in the Cambridge Structural Database (CSD, Version 5.11; Allen, 2002) for 230 other Cu complexes having the same core as (I). In (I), the Cu—N bond lengths involving the peripheral pyridine rings are about 0.1 Å longer than that of the central pyridine ring. These values compare well with those found in a copper complex containing a 4′-p-tolyl-2,2′:6′,2″-terpyridine and two chloride ligands [Cu—N(peripheral) = 2.052 (3) and 2.035 (3) Å, Cu—N(central) =
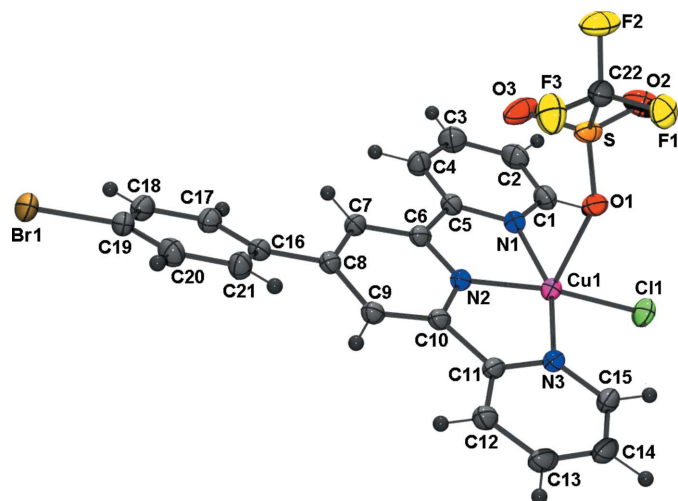

Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.
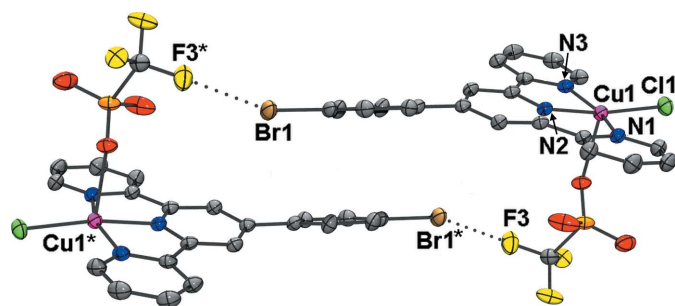
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Figure 2
A view of the dimer formed by halogen-bonding interactions in (I), indicated by dotted lines. [Symmetry code: (*) $-x + 2, -y + 1, -z + 1$.]
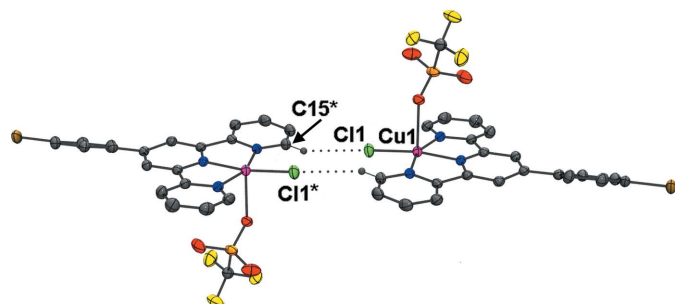

Figure 3
A view of the dimer formed by the C—H···Cl interactions in (I) (dotted lines). [Symmetry code: (*) $-x, -y + 2, -z + 1$.]

1.940 (3) Å and Cu—Cl = 2.228 (1) Å, for the four atoms that form the base of the square-pyramidal coordination around the metal centre; Wang *et al.*, 2009]. On the other hand, the CuN$_6$ core of a homoleptic copper complex exhibits an even greater difference between the peripheral Cu—N and central Cu—N bond lengths [2.205 (4) *versus* 1.981 (5) Å; Uma *et al.*, 2005]. The *trans* N2—Cu1—Cl1 angle in (I) deviates slightly from linearity, while the *cis* N1—Cu1—N2 and N2—Cu1—N3 angles have very similar values deviating by about 10° from 90° because of the bite constrictions of the ligand.

Fig. 1 shows the molecular structure of (I). The axial position of the square-pyramidal Cu^{II} coordination environment is occupied by one O atom of the triflate ligand, with an elongated Cu1—O1 distance of 2.4635 (14) Å. In addition, the triflate ligand extends almost perpendicular to the basal plane of the complex complex, as shown by the Cl1—Cu1—O1 and N2—Cu1—O1 angles (Table 1). Another interesting structural feature of (I) is the dihedral angle of 22.40 (7)° formed between the mean plane through the three pyridine rings and the plane of the bromophenyl group. A similar conformation was found in the two *p*-tolylterpyridine complexes mentioned above (Wang *et al.*, 2009; Uma *et al.*, 2005). The planes of the three pyridyl rings very slightly tilted with respect to each other to give dihedral angles between the pairs of rings containing atoms N1/N2, N2/N3 and N1/N3 of 6.4 (1), 3.7 (1) and 6.1 (1)°, respectively. The tilt between the planes of the central pyridyl and the bromophenyl ring is 24.62 (9)°.
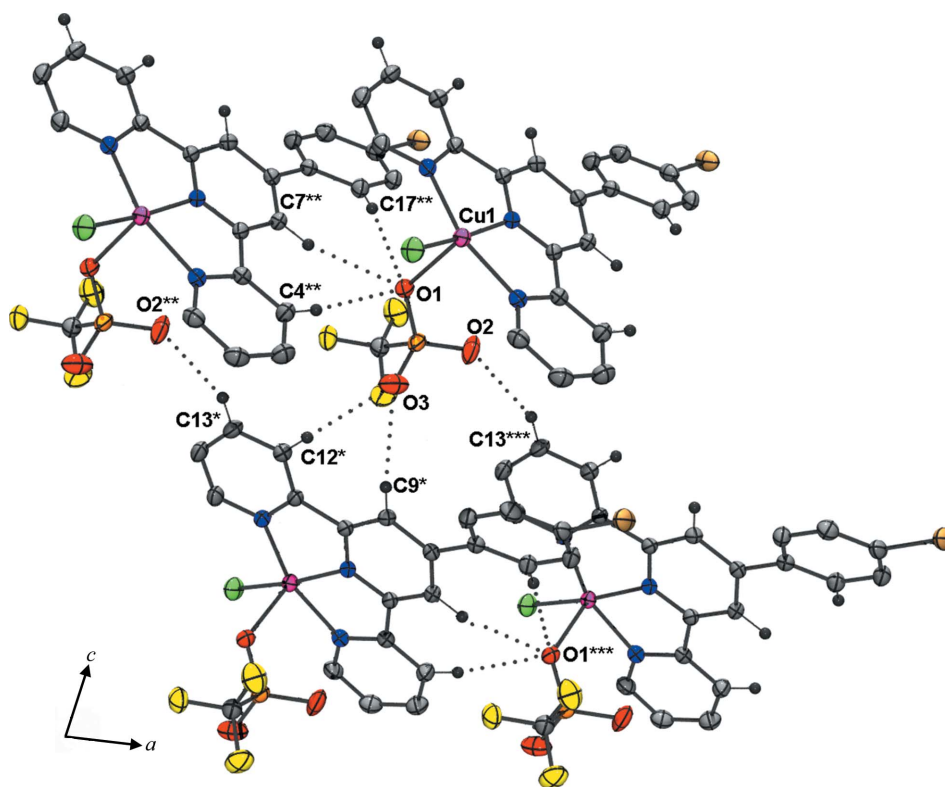

Figure 4
A view of the C—H···O interactions in (I) (dotted lines), showing their influence on the crystal packing and the formation of the supramolecular assembly. [Symmetry codes: (*) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (**) $x - 1, y, z$; (***) $x + \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$.]

As illustrated in Figs. 2–4, the crystal packing of (I) is effected by halogen–halogen interactions and weak hydrogen bonds. In Fig. 2, two molecules are paired by two halogen–halogen interactions to form a dimer about an inversion centre. The shortest intermolecular distance involving F and Br atoms is 3.1482 (14) Å, while the predicted sum of the van der Waals radii for fluorine and bromine is 3.32 Å (Bondi, 1964). Thus, this interaction is rather weak. A survey of similar contacts in the CSD showed 171 reported cases, covering a range of 2.90–3.40 Å with a median (maximum occurrence) at 3.15 Å. Furthermore, the dimeric subunits of (I) are linked to each other across centres of inversion between the dimers by duplex C—H···Cl bonds (Table 2 and Fig. 3) involving the Cl atom and one of the pyridyl rings of the tpy ligand in an adjacent molecule (C15—H; Table 2 and Fig. 3). The C—H···Cl and Br···F interactions serve to link the molecules into extended chains which run parallel to the [2$\overline{1}$0] direction.

Given that (I) has a nearly planar organic ligand, the crystal structure might have been expected to present several aromatic π–π interactions, particularly between the tpy ring systems. However, only one potential interaction is observed, maybe due the blocking caused by the presence of the triflate ligand. The bromophenyl rings from two centrosymmetrically-disposed molecules display a weak π–π interaction such that the centroids of the rings are separated by 3.7333 (11) Å, the perpendicular distance from the centroid of one ring to the plane of the other is 3.4034 (8) Å and the slippage of the centroids is 1.54 Å. Several weak C—H···O interactions (Table 2) appear to provide some support to the vertical alignment of the triflate ligand, and crosslink the above-mentioned chains to give a three-dimensional network. The planarity of the tpy ring system clearly facilitates the formation of these C—H···O interactions (Fig. 4).

In summary, the packing of the title copper complex shows that the presence of the trifluoromethanesulfonate anion plays an active role in the intermolecular interactions. The close Br···F contacts in (I) may be stabilizing interactions but they are apparently not structure determining, since other weak C—H···Cl and C—H···O interactions contribute to the packing pattern.

Experimental

A round-bottomed flask equipped with a stirring bar was charged with $Cu(CF_3SO_3)_2$ (1 equivalent, 0.28 mmol, 101 mg) and bromo-phenylterpyridine (1 equivalent, 0.28 mmol, 109 mg) in acetonitrile (10 ml). To increase the solubility of the organic ligand, chloroform (5 ml) was added to the reaction mixture. The reaction was heated at 358 K for 3 h and then cooled slowly to room temperature under magnetic stirring. Deep-green crystals formed and were filtered off and characterized as the title compound (yield 80 mg; 45%). HRMS (ESI): m/z = 486.93614 ($C_{21}H_{14}BrClCuN_3$ requires 487.25896).

Although the reaction procedure does not involve the chloride anion, it seems that the presence of copper and air photocatalysed the decomposition of the chloroform solvent to form the chloride anion, which was then available to coordinate to the metal centre so as to give rise to the title compound.

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	2.0311 (16)	Cu1—Cl1	2.2048 (5)
Cu1—N2	1.9345 (15)	Cu1—O1	2.4635 (14)
Cu1—N3	2.0338 (16)		
N1—Cu1—Cl1	98.93 (5)	N1—Cu1—N3	159.51 (6)
N2—Cu1—Cl1	169.69 (5)	N2—Cu1—O1	90.92 (5)
N3—Cu1—Cl1	100.24 (5)	N2—Cu1—N3	79.67 (6)
N1—Cu1—O1	95.34 (5)	N3—Cu1—O1	88.61 (5)
N1—Cu1—N2	80.18 (6)	Cl1—Cu1—O1	99.39 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···O1^i	0.95	2.53	3.461 (2)	166
C7—H7···O1^i	0.95	2.66	3.556 (2)	157
C9—H9···O3^{ii}	0.95	2.58	3.451 (2)	152
C12—H12···O3^{ii}	0.95	2.60	3.481 (2)	155
C13—H13···O2^{iii}	0.95	2.32	3.183 (2)	150
C15—H15···Cl1^{iv}	0.95	2.82	3.5696 (19)	137
C17—H17···O1^i	0.95	2.66	3.581 (2)	164

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

Crystal data

[Cu(CF₃O₃S)Cl(C₂₁H₁₄BrN₃)]	$V = 2311.28$ (10) Å³
$M_r = 636.32$	$Z = 4$
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation
$a = 7.7841$ (2) Å	$\mu = 5.78$ mm^{-1}
$b = 16.3043$ (4) Å	$T = 150$ K
$c = 18.2533$ (4) Å	$0.10 \times 0.06 \times 0.06$ mm
$\beta = 93.884$ (1)°	

Data collection

Bruker Microstar diffractometer with a Platinum 135 CCD area detector	47414 measured reflections
	4344 independent reflections
	4016 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$R_{int} = 0.039$
$T_{min} = 0.452$, $T_{max} = 0.707$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	316 parameters
$wR(F^2) = 0.073$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{max} = 0.71$ e Å^{-3}
4344 reflections	$\Delta\rho_{min} = -0.33$ e Å^{-3}

H atoms were generated geometrically, with C—H = 0.95 Å, and were included in the refinement in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *UdMX* (Maris, 2004) and *XPREP* (Bruker, 2008).

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References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Bhaumik, C., Shyamal Das, S., Saha, D., Dutta, S. & Baitalik, S. (2010). *Inorg. Chem.* **49**, 5049–5062.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Bruker (2008). *XPREP*. Version 2008/2. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2009). *APEX2* and *SAINT* (Version 7.68A). Bruker AXS Inc., Madison, Wisconsin, USA.

Chen, X., Huang, Z., Chen, S.-Y., Kun Li, K., Yu, X.-Q. & Pu, L. (2010). *J. Am. Chem. Soc.* **132**, 7297–7299.

Han, F. S., Higuchi, M. & Kurth, D. G. (2008). *J. Am. Chem. Soc.* **130**, 2073–2081.

Maris, T. (2004). *UdMX*. University of Montréal, Canada.

McMurtrie, J. & Dance, I. (2009). *CrystEngComm*, **11**, 1141–1149.

Medlycott, E. A., Hanan, G. S., Abedin, T. S. M. & Thompson, L. K. (2008). *Polyhedron*, **27**, 493–501.

Medlycott, E. A., Udachin, K. A. & Hanan, G. S. (2007). *Dalton Trans*. pp. 430–438.

Rajeshwar, K., McConnell, R. & Licht, S. (2008). In *Solar Hydrogen Generation Toward a Renewable Energy Future*. New York: Springer.

Sheldrick, G. M. (1996). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Uma, V., Vaidyanathan, V. G. & Nair, B. U. (2005). *Bull. Chem. Soc. Jpn*, **78**, 845–850.

Wang, S., Li, B.-D., Wang, R. Y., Wu, B. L. & Zhang, H.-Y. (2009). *Synth. React. Inorg. Met. Org. Nano-Met. Chem.* **39**, 355–359.