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Key indicators

Single-crystal X-ray study
T = 294 K
Mean $\sigma(C-C) = 0.005 \text{ \AA}$
Disorder in solvent or counterion
R factor = 0.047
wR factor = 0.102
Data-to-parameter ratio = 10.6

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

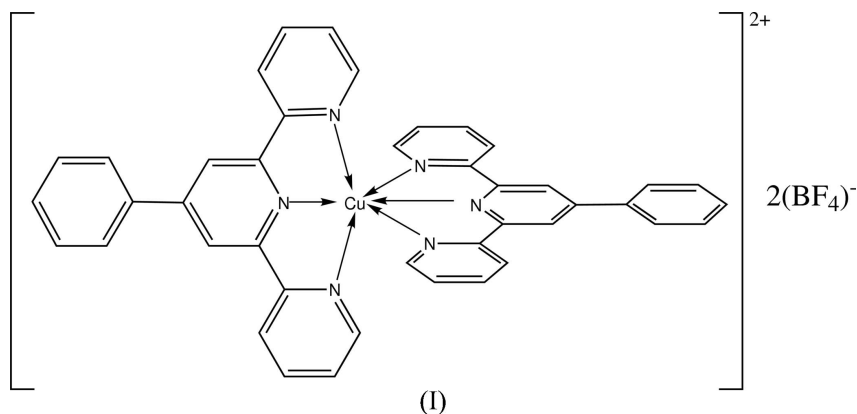
Bis(4'-phenyl-2,2':6',2''-terpyridine- $\kappa^3 N, N', N''$)-copper(II) bis(tetrafluoroborate)

The 4-phenylterpyridine ligand coordinates to the Cu^{II} ion in the title compound, $[\text{Cu}(\text{C}_{21}\text{H}_{15}\text{N}_3)_2](\text{BF}_4)_2$, as an N, N', N'' -terdentate meridional ligand. The geometry of the Cu atom in the cation is octahedral. The BF_4^- anions are disordered.

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Comment

4'-Phenyl-2,2':6',2''-terpyridine (Ph-terpy) has been used as a ligand with different metal ions, and a monomeric Zn^{II} compound (Tu *et al.*, 2004), as well as polymeric compounds with Zn^{II} (Tu, Yin, He *et al.*, 2005) and Cu^{II} (Tu, Yin, Li *et al.*, 2005), have been reported. As part of a research study devoted to the possible use of $\pi-\pi$ interactions arising from heterocyclic rings as a tool for the designed synthesis of molecular networks, we synthesized the title compound, (I), for a crystal structure study.



The asymmetric unit of (I) consists of an octahedral $[\text{Cu}(\text{Ph-terpy})_2]^{2+}$ ion and two disordered BF_4^- anions. The Ph-terpy ligands coordinate as N, N', N'' -terdentate ligands in a meridional configuration. The Cu–N distance to the central pyridine ring is significantly shorter than the distances to the outer pyridine rings (Table 1), indicating a compressed octahedral geometry. The N–Cu distances are within the values reported in the Cambridge Structural Database (CSD, Version 5.26; Allen, 2002) for $[\text{Cu}(\text{NNN})_2]^{2+}$ compounds with NNN being terpy- and Ph-terpy-type ligands. In these compounds the lateral pyridine N–Cu distance ranges from 2.059 to 2.335 Å with a mean value of 2.18 (7) Å; the middle pyridine Cu–N distance ranges from 1.915 to 2.009 Å with a mean of 1.98 (3) Å [terpy ligand CSD refcodes: BEJPUB (Arriortua *et al.*, 1982), BEJPUB01 (Olmstead, *et al.*, 2004), NELKEU (Valdés-Martínez *et al.*, 2001), SIBWEF (Folgado *et al.*, 1990) and TERPYC01 (Allmann, *et al.*, 1978); Ph-terpy ligand refcodes: KOFQAX (Alcock *et al.*, 2000), NIQTAI (Storrier *et*

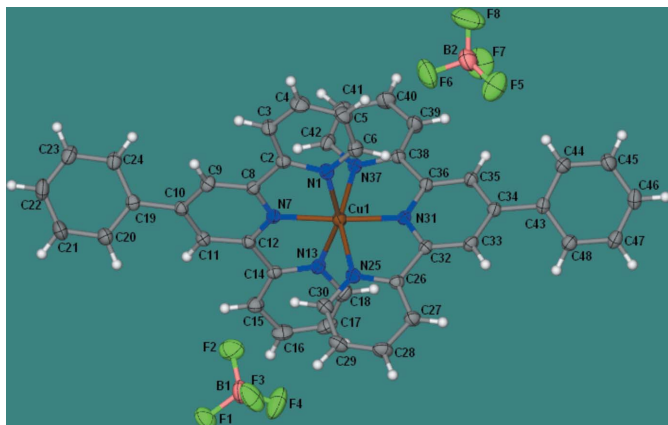


Figure 1

A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level; H atoms are shown as circles of arbitrary radii. Only the major components of disordered atoms are shown.

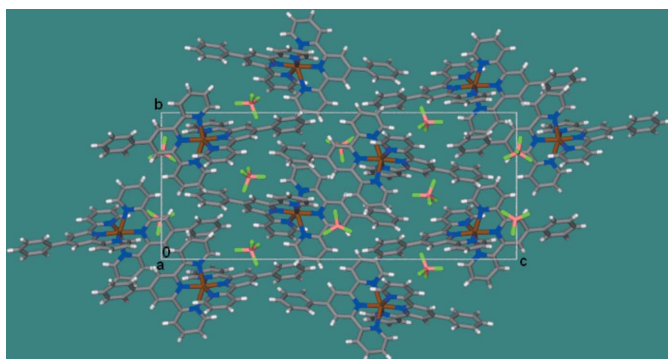


Figure 2

A molecular packing diagram of (I), viewed down the *a* axis. Only the major components of disordered atoms are shown.

al., 1997), PULCAA (Whittle *et al.*, 1998) and SIMJAZ (Storrier *et al.*, 1998)].

The terpy portion of the Ph-terpy ligands deviates from planarity as indicated by the N–C–C–N torsion angles (Table 1). The phenyl rings are twisted significantly from the terpy group; the angles between the mean planes of the phenyl rings C19–C24 and C43–C48 and the mean planes of the py rings to which they are attached are 32.5 (2) and 45.5 (2)°, respectively.

The molecules pack as shown in Fig. 2. The only possible π – π interaction within accepted centroid–centroid values (Janiak, 2000) is between the pyridyl ring N37/C38–C42 and the phenyl ring C43–C48 of the molecule generated by the symmetry code $(-x, \frac{1}{2} + y, \frac{1}{2} - z)$ (3.890 Å); however, the distance is at the upper limit and the rings are not parallel [dihedral angle between planes: 10.6 (2)°]. Contrary to what is observed for bis(2,2';6,2'-terpyridyl) metal complexes functionalized with biphenyl 'tails', where coordination polymers assembled through π – π interactions were obtained (Alcock *et al.*, 2000), the π – π interactions in (I) are not capable of overcoming the collective directional 'packing forces' influencing the molecular arrangement in the crystal structure.

Experimental

4'-Phenyl-2,2':6',2''-terpyridine was synthesized according to a published procedure (Constable *et al.*, 1990). An aqueous solution (10 ml) of copper(II) tetrafluoroborate hydrate (23.72 mg, 0.10 mmol) was added to an ethanol solution (10 ml) of 4'-phenyl-2,2':6',2''-terpyridine (30.9 mg, 0.10 mmol), forming a light-blue solution. Blue crystals suitable for X-ray structure determination were obtained by slow evaporation after three days at room temperature.

Crystal data

[Cu(C₂₁H₁₅N₃)₂](BF₄)₂
M_r = 855.88
 Monoclinic, *P*2₁/*c*
a = 9.4054 (4) Å
b = 12.8726 (6) Å
c = 31.520 (1) Å
 β = 98.354 (1)°
V = 3775.7 (3) Å³
Z = 4

D_x = 1.506 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 7974 reflections
 θ = 2.4–24.7°
 μ = 0.66 mm⁻¹
T = 294 (2) K
 Prism, blue
 0.27 × 0.16 × 0.10 mm

Data collection

Bruker SMART APEX CCD diffractometer
 ω scans
 Absorption correction: analytical (SHELXTL; Sheldrick, 2000)
T_{min} = 0.849, *T_{max}* = 0.947
 30307 measured reflections

6637 independent reflections
 4253 reflections with *I* > 2 σ (*I*)
R_{int} = 0.056
 θ_{max} = 25.0°
h = -11 → 11
k = -15 → 15
l = -37 → 37

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.047
wR (*F*²) = 0.102
S = 0.88
 6637 reflections
 624 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0481P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.48 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{min} = -0.46 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Cu1–N31	1.954 (3)	Cu1–N37	2.139 (3)
Cu1–N7	2.004 (3)	Cu1–N13	2.217 (3)
Cu1–N25	2.130 (3)	Cu1–N1	2.231 (3)
N31–Cu1–N7	173.76 (11)	N25–Cu1–N13	87.02 (11)
N31–Cu1–N25	78.29 (11)	N37–Cu1–N13	96.19 (10)
N7–Cu1–N25	101.97 (10)	N31–Cu1–N1	97.15 (11)
N31–Cu1–N37	78.13 (10)	N7–Cu1–N1	76.61 (11)
N7–Cu1–N37	102.03 (10)	N25–Cu1–N1	97.15 (10)
N25–Cu1–N37	155.87 (11)	N37–Cu1–N1	90.76 (10)
N31–Cu1–N13	109.75 (11)	N13–Cu1–N1	153.05 (11)
N7–Cu1–N13	76.47 (11)		
N1–C2–C8–N7	–4.1 (5)	N25–C26–C32–N31	–7.5 (5)
N7–C12–C14–N13	–7.4 (5)	N31–C36–C38–N37	6.1 (5)

H atoms were located in a difference Fourier map and refined as riding [C–H = 0.93 Å and *U_{iso}*(H) = 1.2*U_{eq}*(C)]. Both BF₄ anions were found to be disordered over (at least) two sites with occupation factors of 0.554 (5) and 0.446 (5) for B1/F1–F4 and 0.520 (8) and 0.480 (8) for B2/F5–F8. A split model with restrained B–F and F–F distances was introduced.

Data collection: SMART (Bruker, 1999); cell refinement: SAINT-Plus (Bruker, 1999); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXTL (Sheldrick, 2000); program(s) used to

refine structure: *SHELXTL*; molecular graphics: *X-SEED* (Version 2.0; Barbour, 2001); software used to prepare material for publication: *SHELXTL* and *enCIFer* (Allen *et al.*, 2004).

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References

- Alcock, N. W., Barker, P. R., Haider, J. M., Hannon, M. J., Painting, C. L., Pikramenou, Z., Plummer, E. A., Rissanen, K. & Saarenketo, P. (2000). *J. Chem. Soc. Dalton Trans.* pp. 1447–1461.
- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.
- Allmann, R., Henke, V. & Reinen, V. (1978). *Inorg. Chem.* **17**, 378–382.
- Arriortua, M. I., Rojo, V., Amigo, V., Germain, G. & Declercq, J. P. (1982). *Acta Cryst.* **B38**, 1323–1324.
- Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
- Bruker (1999). *SMART* (Version 5.625) and *SAINT-Plus* (Version 6.23C). Bruker AXS Inc., Madison, Wisconsin, USA.
- Constable, E. C., Lewis, J., Liptrot, M. C. & Raithby, P. R. (1990). *Inorg. Chim. Acta*, **178**, 47–54.
- Folgado, J.-V., Henke, W., Allmann, R., Stratemeier, H., Beltran-Porter, D., Rojo, T. & Reinen, D. (1990). *Inorg. Chem.* **29**, 2035–2042.
- Janiak, C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3885–3896.
- Olmstead, M. M., Safari, N., Haddadzadeh, H. & Rezvani, A.-R. (2004). Private Communication.
- Sheldrick, G. M. (2000). *SHELXTL*. Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA.
- Storrier, G. D., Colbran, S. B. & Craig, D. C. (1997). *J. Chem. Soc. Dalton Trans.* pp. 3011–3028.
- Storrier, G. D., Colbran, S. B. & Craig, D. C. (1998). *J. Chem. Soc. Dalton Trans.* pp. 1351–1364.
- Tu, Q.-D., Li, D., Wu, T., Yin, Y.-G. & Ng, S. W. (2004). *Acta Cryst.* **E60**, m1403–m1404.
- Tu, Q.-D., Yin, Y.-G., He, J., Xiang, J., Li, D. & Ng, S. W. (2005). *Acta Cryst.* **E61**, m254–m256.
- Tu, Q.-D., Yin, Y.-G., Li, D., Huang, X.-C. & Ng, S. W. (2005). *Acta Cryst.* **E61**, m103–m105.
- Valdés-Martínez, J., Toscano, R. A. & Salazar-Mendoza, D. (2001). *Acta Cryst.* **E57**, m331–m332.
- Whittle, B., Horwood, E. L., Rees, L. H., Batten, S. R., Jeffery, J. C. & Ward, M. D. (1998). *Polyhedron*, **17**, 373–380.