Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

(Acetonitrile)(6,6″-dimesityl-2,2′:6′,2″-terpyridine)copper(I) hexafluorophosphate

Akira Onoda, Keiko Kawakita, Taka-aki Okamura, Hitoshi Yamamoto and Norikazu Ueyama*

Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

Correspondence e-mail: ueyama@chem.sci.osaka-u.ac.jp

Received 1 April 2003
Accepted 14 April 2003
Online 23 April 2003

Key indicators

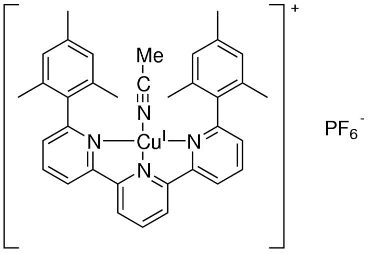
Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.012 Å
R factor = 0.052
wR factor = 0.227
Data-to-parameter ratio = 17.2

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

The title compound, [Cu^I(dmtpy)(NCMe)](PF_6) (dmtpy = 6,6″-dimesityl-2,2′:6′,2″-terpyridine) or [$Cu(C_2H_3N)(C_{33}H_{31}N_3)$]($PF_6$), displays a distorted square-planar coordination, with four N atoms from dmtpy and acetonitrile molecules, as a result of the extremely bulky terpyridyl ligand.

Comment

The design of N-chelating ligands with various bulky substituents is an essential approach in developing N-chelating metal catalysts for polymerization. For example, Johnson *et al.* (1995) have reported highly efficient Pd and Ni catalysts, with α-diimino ligands, for the polymerization of ethylene and α-olefins. It was also reported that control the bulkiness in pyridine bisimino ligands (3N coordination) contributes to polymerization by their Fe and Co catalysts (Small *et al.*, 1998; Britovsek *et al.*, 1998). We have determined the crystal structure of the title compound, (I), to show the effect of the steric hindrance of the bulky terpyridine ligand 6,6″-dimesityl-2,2′:6′,2″-terpyridine (dmtpy), perturbing the metal coordination geometry.



(I)

The Cu complex in (I) displays a distorted square-planar coordination, with four N atoms from dmtpy and acetonitrile molecules, as a result of the extremely bulky terpyridyl ligand. The Cu1—N21 bond distance of 2.003 (5) Å for the central pyridine ring is shorter than those for the pyridine rings of both sides, 2.232 (5) Å and 2.244 (5) Å (Table 1). The Cu atom is almost coplanar with the central pyridine ring [C24···N21—Cu1, 176.8 (3)°]. For the pyridine rings on either side C14···N11—Cu1 is 155.7 (3)° and C34···N31—Cu1 is 158.7 (3)°. The N21—Cu1—N1 bond angle is 152.8 (3)° and the Cu atom is located 0.625 (1) Å from the N11/N21/N31 plane. The bulkiness of dimesityl groups in the 6,6″-positions of terpyridine ligand disrupts the square-planar coordination geometry towards a highly distorted tetrahedral one. Our design of bulky derivatives of terpyridine ligands successfully induces a distortion in the Cu^I coordination geometry (Fig. 2).

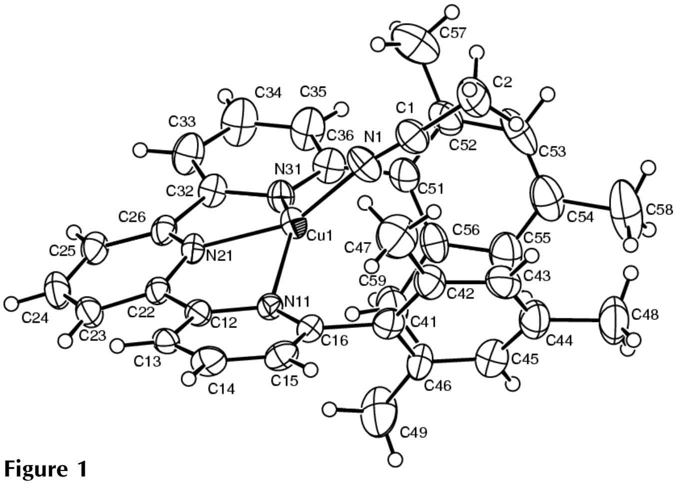


Figure 1
The structure of the complex cation in (I), showing the labeling and 25% probability ellipsoids for non-H atoms.

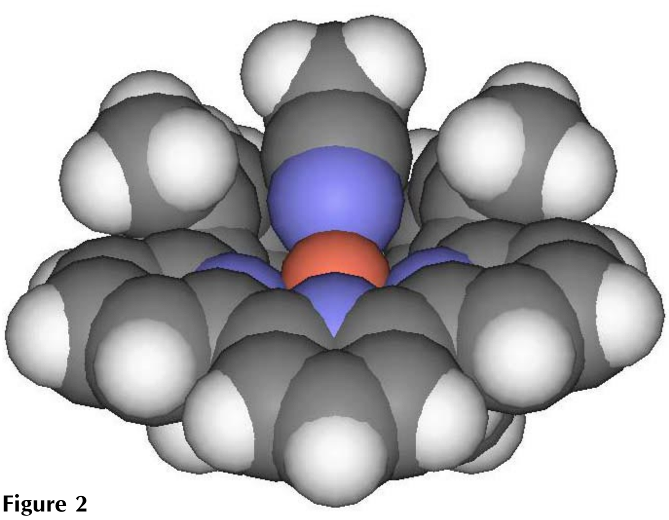


Figure 2
Space-filling model of the cation of (I). Color scheme: brown (Cu), purple (N) and black (C).

Experimental

To a solution of dmtpy (286 mg, 0.61 mmol) in tetrahydrofuran (12 ml) was added a solution of $[Cu(NCMe)_4](PF_6)$ (226 mg, 0.61 mmol) in MeCN (5 ml) at room temperature. The reaction mixture was stirred for 10 min and dried in vacuo. The residue was recrystallized from MeCN/ether to give dark red crystals of (I). Yield: 26 mg (6.2%). Elemental analysis, calculated for $C_{35}H_{34}CuF_6N_4P$: C 58.45, H 4.77, N 7.79%; found: C 58.78, H 4.50, N 7.88%.

Crystal data

$[Cu(C_2H_3N)(C_{33}H_{31}N_3)](PF_6)$
$M_r = 719.17$
Monoclinic, $P2_1/n$
$a = 11.317$ (3) Å
$b = 23.592$ (4) Å
$c = 12.873$ (2) Å
$\beta = 92.450$ (16)°
$V = 3433.7$ (11) Å^3
$Z = 4$

$D_x = 1.391$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 29.2$–30.0°
$\mu = 0.75$ mm^{-1}
$T = 296$ K
Block, dark red
0.50 × 0.30 × 0.20 mm

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.842$, $T_{\max} = 0.998$
7686 measured reflections
7302 independent reflections
2104 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.150$
$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 30$
$l = -16 \rightarrow 16$
3 standard reflections every 150 reflections intensity decay: 0.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.227$
$S = 0.91$
7302 reflections
425 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.50$ e Å^{-3}
$\Delta\rho_{\min} = -0.58$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.886 (6)	Cu1—N31	2.232 (5)
Cu1—N21	2.003 (5)	Cu1—N11	2.244 (5)
N1—Cu1—N21	152.8 (3)	N1—Cu1—N11	106.8 (2)
N1—Cu1—N31	108.8 (2)	N21—Cu1—N11	76.8 (2)
N21—Cu1—N31	76.3 (2)	N31—Cu1—N11	142.9 (2)

H atoms were positioned geometrically and were treated as riding on their parent C atoms, with aromatic C—H distamces of 0.93 Å and methyl C—H distances of 0.96 Å. Rotating group refinement was used for the methyl groups.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *TEXSAN* and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL*97.

Support of this work by JSPS Fellowships [for AO; grant 2306(1999–2002)] and a Grant-in-Aid for Scientific Research on Priority Area (A) (No. 10146231) from the Ministry of Education, Science, Sports and Culture, Japan, is gratefully acknowledged.

References

Britovsek, G. J. P., Gibson, V. C., Kimberley, B. S., Maddox, P. J., McTavish, S. J., Solan, G. A., White, A. J. P. & Williams, D. J. (1998). *Chem. Commun.* pp. 849–850.
Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.
Johnson, L. K., Killiam, C. M. & Brookhart, J. (1995). *J. Am. Chem. Soc.* **117**, 6414–6415.
Molecular Structure Corporation (1991). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1999). *TEXSAN*. Version 1.10. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
North, A. C. T., Phillips, D. C., & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXL*97. University of Göttingen, Germany.
Small, B. L., M., Brookhart, J. & Bennett, A. M. (1998). *J. Am. Chem. Soc.* **120**, 4049–4050.

Acta Cryst. (2003). E**59**, m266–m267 Akira Onoda *et al.* • $[Cu(C_2H_3N)(C_{33}H_{31}N_3)](PF_6)$ **m267**