Bis{μ:κ²,κ²-6,6′-bis[2-(2-pyridyl)ethyliminomethyl]-2,2′-bipyridine}dicopper(I) bis(hexafluorophosphate)

Dietmar Kennepohl,[a]*
Angela Thomas[a] and
Robert McDonald[b]‡

[a]Athabasca University, 1 University Drive, Athabasca, Alberta, Canada T9S 3A3, and [b]Chemistry Department, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

‡ X-ray Crystallography Laboratory.

Correspondence e-mail: dietmark@athabascau.ca

Key indicators

Single-crystal X-ray study
$T = 193$ K
Mean σ(C–C) = 0.005 Å
R factor = 0.045
wR factor = 0.130
Data-to-parameter ratio = 15.1

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

In the structure of the title compound, $[Cu_2(C_{26}H_{24}N_6)_2](PF_6)_2$, the Cu atoms of the cation are located on a twofold axis, and adopt a distorted tetrahedral coordination geometry. The terminal 2-(2-pyridyl)ethyl groups are not coordinated to the metal centers.

Comment

Lehn and others have strongly promoted the idea of creating intricate nanosized supramolecular devices in a single step from a mixture of suitably tailored molecular components (Constable, 1994; Lehn, 1994). The prospect of complex supramolecular architectures being self-assembled from simple components by careful design of those components is very exciting and opens the possibility of accessing interesting extended systems. The structure and properties of self-assembled multinuclear metal complexes have attracted particular attention owing to their interesting physiochemical features such as redox potentials, as well as a variety of optical and magnetic properties (Gütlich *et al.*, 2000; Bünzli & Piguet, 2002; Xu *et al.*, 2002, and references therein). The aim is to initially form smaller systems for study in understanding and modeling of the more extended systems. To this end, we have designed and prepared a chelating ligand system having only N donor atoms. The simple Schiff base condensation reaction of a dialdehyde, 2,2′-bipyridine-6,6′-dicarbaldehyde, with two equivalents of a primary amine, 2-(2-pyridyl)ethylamine, yields the ligand *L* . Reaction of *L* with an equimolar amount of CuPF$_6$ yields the dinuclear complex $[Cu_2\{\mu:\kappa^2,\kappa^2$-6,6′-bis[2-(2-pyridyl)ethylminomethyl]-2,2′-bipyridine$\}_2][PF_6]_2$, (I) (the complex can also be formed by combining the dialdehyde, the amine and CuPF$_6$ in solution). The structure of the complex cation is shown in Fig. 1.
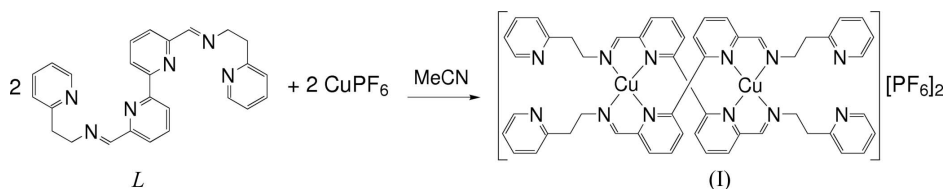
The copper centers are located on a twofold axis $(0, y, \frac{1}{4})$ and the ligands are arranged in helical fashion. A pyridyl N atom and an imine N atom from each ligand are coordinated to each copper center, while the terminal 2-(2-pyridyl)ethyl groups are uncoordinated to any metal center and form no notable intermolecular interactions. Bond distances and angles about the copper centers are given in Table 1. For both metal centers the Cu—N(imine) distances (Cu1—N11 and
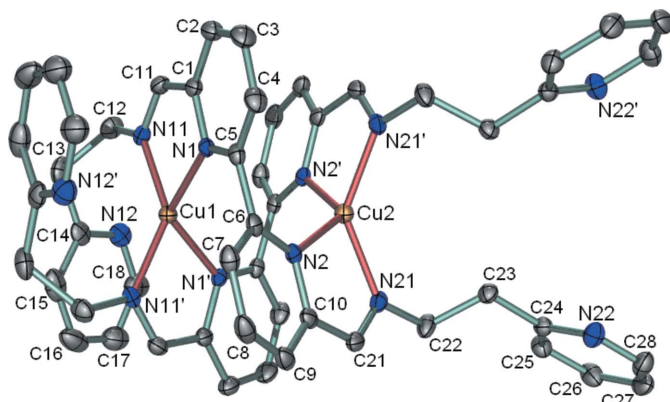
Figure 1
The structure of the [Cu$_2${μ:κ^2,κ^2-6,6′-bis[2-(2-pyridyl)ethyliminomethyl]-2,2′-bipyridine}$_2$]$^{2+}$ ion. Displacement ellipsoids for non-H atoms are shown at the 30% probability level (H atoms have been omitted). Primed atoms are related to unprimed ones by the operation (−x, y, ½ − z).

Cu2—N21) are slightly shorter than the Cu—N(pyridyl) distances (Cu1—N1 and Cu2—N2). The coordination geometry about each metal is significantly distorted from tetrahedral, with the ligand chelate angles (N1—Cu1—N11 and N2—Cu2—N21) and the imine–copper–imine angles (N11—Cu1—N11′ and N21—Cu2—N21′; primed atoms are related to unprimed ones via the aformentioned twofold axis) showing the largest deviations from the ideal.

Experimental

For the preparation of 6,6′-bis[(2-pyridyl)ethyliminomethyl]-2,2′-bipyridine (*L*), 2,2′-bipyridine-6,6′-dicarbaldehyde was prepared using a modified version of the published method (Parks *et al.*, 1973). Neat 2-(2-pyridyl)ethylamine (1.51 g, 12.3 mmol, 1.47 ml) was added *via* a syringe to a solution of 2,2′-bipyridine-6,6′-dicarbaldehyde (1.31 g, 6.16 mmol) in anhydrous ethanol (50 ml). After 30 min stirring at room temperature, enough additional EtOH was added to dissolve the precipitate that had formed, and the solution was heated to boiling to encourage complete reaction. The clear light-yellow solution was allowed to cool to room temperature, with colorless microcrystals forming after 1 h. The reaction mixture was further cooled to 277 K, and after 2 h the crystals were collected *via* suction filtration and washed with Et$_2$O. A second crop was obtained by reducing the volume of the filtrate and cooling to 243 K. The amounts obtained were combined and dried *in vacuo*, yielding 2.17 g (84%) of colorless microcrystalline product (m.p. 422–424 K). IR: ν(C≡N) 1650 cm^{-1}. Analysis calculated for C$_{26}$H$_{24}$N$_6$: C 74.26, H 5.75, N 19.98%; found: C 74.22, H 5.61, N 19.93%.

For the preparation of (I), a solution of CuPF$_6$ (80.7 mg, 0.217 mmol) in acetonitrile (20 ml) was degassed under an N$_2$ stream for 10 min. Upon addition of solid 6,6′-bis[(2-pyridyl)ethyliminomethyl]-2,2′-bipyridine (92.5 mg, 0.220 mmol), the mixture turned dark green/black and was stirred at room temperature. Crystals were grown *via* closed-chamber vapor diffusion of diethyl ether into this solution; the crystals appeared as very dark-green prisms after 3 d. They were removed from the solvent and washed with diethyl ether, then air-dried (total yield 197 mg, 72%, m.p. 511–513 K). IR: ν(C≡N) 1624 cm^{-1}. Analysis calculated for C$_{52}$H$_{48}$Cu$_2$F$_{12}$N$_{12}$P$_2$: C 49.65, H 3.85, N 13.36%; found: C 49.63, H 3.74, N 13.39%. Positive

electrospray mass spectrometry (with CH$_3$CN) gave a strong peak at *m/z* = 483, corresponding to the fragment {C$_{26}$H$_{24}$N$_6$Cu$^+$}; a weaker signal at *m/z* = 1113 suggested the presence of [C$_{26}$H$_{24}$N$_6$]$_2$Cu$_2$PF$_6$$^+$.

Crystal data

[Cu(C$_{26}$H$_{24}$N$_6$)$_2$](PF$_6$)$_2$	$Z = 4$
$M_r = 1258.04$	$D_x = 1.565$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 13.6325$ (7) Å	$\mu = 0.95$ mm^{-1}
$b = 16.6329$ (9) Å	$T = 193$ (2) K
$c = 23.8071$ (12) Å	Prism, dark green
$\beta = 98.3298$ (10)°	$0.48 \times 0.29 \times 0.15$ mm
$V = 5337.7$ (5) Å^3	

Data collection

Bruker SMART 1000 CCD area-detector/PLATFORM diffractometer	16047 measured reflections 5470 independent reflections 4525 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.032$
Absorption correction: multi-scan (*SADABS*; Bruker, 2003) $T_{min} = 0.659$, $T_{max} = 0.871$	$\theta_{max} = 26.4°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0733P)^2 + 9.7413P]$
$R[F^2 > 2\sigma(F^2)] = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.130$	
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.001$
5470 reflections	$\Delta\rho_{max} = 1.13$ e Å^{-3}
362 parameters	$\Delta\rho_{min} = -0.47$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	2.074 (2)	Cu2—N2	2.070 (2)
Cu1—N11	2.036 (2)	Cu2—N21	2.010 (2)
N1—Cu1—N1^i	125.03 (12)	N2—Cu2—N2^i	124.63 (12)
N11—Cu1—N1	80.72 (9)	N2—Cu2—N21	81.09 (10)
N1—Cu1—N11^i	117.48 (9)	N2—Cu2—N21^i	119.12 (9)
N11—Cu1—N11^i	142.05 (13)	N21^i—Cu2—N21	138.15 (14)

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

H atoms were placed in idealized positions (C—H = 0.95–0.99 Å) and these were assigned U_{iso} values of 1.2 times U_{eq} of the parent C atoms. The highest peak of residual electron density is located 1.11 Å from F1 and is of no chemical significance.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *DIRDIF96* (Beurskens *et al.*, 1996); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *POV-RAY* for Windows (The POV-RAY Team, 2002); software used to prepare material for publication: *SHELXTL* (Bruker, 2003).

References

Beurskens, P. T., Beurskens, G., Bosman, W. P., de Gelder, R., Garcia Granda, S., Gould, R. O., Israel, R. & Smits, J. M. M. (1996). *DIRDIF96*. University of Nijmegen, The Netherlands.
Bruker (2001). *SMART*. Version 5.054. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2003). *SADABS* (Version 2.10), *SAINT* (Version 7.06A) and *SHELXTL* (Version 6.14). Bruker AXS Inc., Madison, Wisconsin, USA.

Bünzli, J.-C. G. & Piguet, C. (2002). *Chem. Rev.* **102**, 1897–1928.

Constable, E. C. (1994). *Progress in Inorganic Chemistry*, Vol. 42, edited by K. D. Karlin, pp. 67–138. New York: John Wiley & Sons.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Gütlich, P., Garcia, Y. & Goodwin, H. A. (2000). *Chem. Soc. Rev.* **29**, 419–427.

Lehn, J.-M. (1994). *Supramolecular Chemistry: Concepts and Perspectives*, ch. 9. Weinheim: VCH.

Parks, J. E., Wagner, B. E. & Holm, R. H. (1973). *J. Organomet. Chem.* **56**, 53–66.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

The POV-RAY Team (2002). *POV-RAY* for Windows. http://www.povray.org/download/.

Xu, Z., Thompson, L. K. & Miller, D. O. (2002). *J. Chem. Soc. Dalton Trans.* pp. 2462–2466.