Bis[μ-bis(diphenylphosphino)methane-κ²P:P']bis[diacetonitrilecopper(I)] bis(hexafluorophosphate)

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Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(C–C) = 0.011 Å
R factor = 0.068
wR factor = 0.169
Data-to-parameter ratio = 14.3

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

The title compound, $[Cu_2(\mu_2\text{-dppm})_2(MeCN)_4](PF_6)_2$ or $[Cu_2(C_{25}H_{22}P_2)_2(C_2H_3N)_4](PF_6)_2$, crystallizes in the monoclinic space group $C2/c$, with the cation on a twofold axis. The Cu centers are four-coordinated, exhibiting pseudo-tetrahedral coordination.

Comment

The diphosphine bis(diphenylphosphino)methane (dppm) is widely used to design coinage metal complexes owing to its good bridging properties (Diez *et al.*, 1987). The binuclear compounds $[M_2(\mu_2\text{-dppm})_2]$ usually display eight-membered rings (Yang *et al.*, 1997), as in $[Au_2(\mu_2\text{-dppm})_2][Au(GeCl_3)_2]_2$ (Bauer & Schmidbaur, 1997), $[Ag_2(\mu_2\text{-dppm})_2](ClO_4)_2$ (Ahrens & Jones, 1998) and $[Cu_2(\mu_2\text{-dppm})_2(MeCN)_4](ClO_4)_2$ (Diez *et al.*, 1987). This paper describes the crystal structure of a copper-based system, (I), with PF_6^- as the anion.

(I)
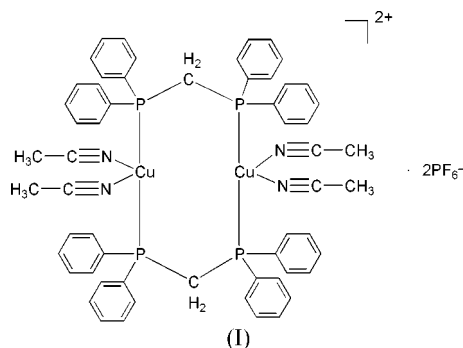
The complex consists of the dication $[Cu_2(\mu_2\text{-dppm})_2(MeCN)_4]^{2+}$, situated on a twofold axis, and two PF_6^- anions. A perspective drawing of the complex with the atomic numbering scheme is depicted in Fig. 1. Selected bond lengths and angles are presented in Table 1. The two Cu atoms are doubly bridged by dppm ligands to give an eight-membered ring, $[Cu_2(\mu_2\text{-dppm})_2]$. The Cu centers adopt a distorted tetrahedral geometry in which the four coordination sites around the copper are occupied by two P atoms of dppm and two N atoms from acetonitrile. The Cu···Cu distance of 3.756 (1) Å is longer than that in $[Cu_2(\mu_2\text{-dppm})_2(MeCN)_4](ClO_4)_2$, 3.426 (3) Å; this may be due to the Cu–anion interaction. The Cu—P distances are 2.2730 (14) and 2.2859 (15) Å, which are close to those in the above-mentioned compound. The acetonitrile ligands, on the other hand, are quite different, with one being nearly linear [C1—N1—Cu1 = 171.8 (6)°] and the other bent [C3—N2—Cu1 = 157.5 (6)°]. The corresponding Cu—N bond lengths are also different, with N1—Cu1 [2.031 (5) Å] being shorter than N2—Cu1 [2.172 (5) Å].

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Experimental

A mixture of $[Cu(MeCN)_4](PF_6)_2$ (Shriver, 1979) and dppm in a 1:1 ratio in dichloromethane was stirred under an inert atmosphere at room temperature overnight. Concentration of the solution and addition of diethyl ether resulted in the precipitation of an off-white solid. Well shaped colorless crystals suitable for X-ray diffraction measurement were grown by slow diffusion of diethyl ether into an acetonitrile solution at room temperature.

Crystal data

$[Cu_2(C_{25}H_{22}P_2)_2(C_2H_3N)_4](PF_6)_2$	$D_x = 1.476$ Mg m^{-3}
$M_r = 1349.97$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 4793
$a = 22.5125 (3)$ Å	reflections
$b = 13.1916 (2)$ Å	$\theta = 1.8–25.0°$
$c = 21.6096 (3)$ Å	$\mu = 0.94$ mm^{-1}
$\beta = 108.748 (1)°$	$T = 293 (2)$ K
$V = 6077.02 (15)$ Å^3	Block, colorless
$Z = 4$	$0.60 \times 0.56 \times 0.56$ mm

Data collection

Siemens SMART 1K CCD diffractometer	5273 independent reflections
	4180 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.025$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 25.0°$
	$h = -26 \rightarrow 23$
$T_{min} = 0.561$, $T_{max} = 0.592$	$k = -15 \rightarrow 13$
8897 measured reflections	$l = -10 \rightarrow 25$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0384P)^2 + 40.8701P]$
$R[F^2 > 2\sigma(F^2)] = 0.068$	
$wR(F^2) = 0.169$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.23$	$(\Delta/\sigma)_{max} < 0.001$
5273 reflections	$\Delta\rho_{max} = 0.55$ e Å^{-3}
368 parameters	$\Delta\rho_{min} = -0.66$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	2.031 (5)	Cu1—P1	2.2730 (14)
Cu1—N2	2.172 (6)	Cu1—P2	2.2859 (15)
N1—Cu1—N2	95.6 (2)	C121—P1—Cu1	109.52 (17)
N1—Cu1—P1	117.74 (14)	C01^i—P1—Cu1	116.46 (18)
N2—Cu1—P1	101.79 (14)	C211—P2—Cu1	116.35 (19)
N1—Cu1—P2	117.24 (15)	C01—P2—Cu1	120.26 (17)
N2—Cu1—P2	95.01 (15)	C1—N1—Cu1	171.8 (6)
P1—Cu1—P2	119.99 (6)	C3—N2—Cu1	157.5 (6)

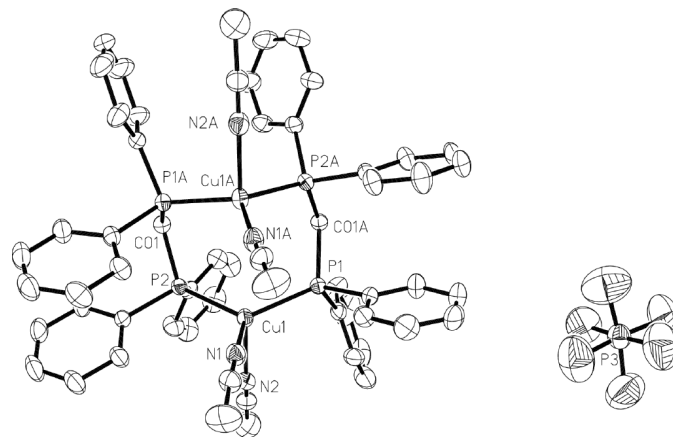Symmetry code: (i) $1-x, y, \frac{3}{2}-z$.

Figure 1
A view of the title complex, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted. Only key atoms are labeled, and the suffix *A* corresponds to symmetry code (i) in Table 1

The H atoms were positioned geometrically (C—H = 0.96 Å), assigned isotropic displacement parameters and allowed to ride on their respective parent C atoms.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART* and *SAINT* (Siemens, 1994); data reduction: *SAINT* and *XPREP* in *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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