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μ-4,4′-Di-4-pyridyldiazene-κ^2N:N'-bis{[1,1,1-tris(diphenylphosphinomethyl)ethane-κP^3]copper(I)} bis(tetrafluoroborate) dichloromethane solvate

Ming-Ming Yu,[a] Zhan-Xian Li,[a] Wen-Fu Fu[a,b]* and Jun-Feng Zhang[a,a]

[a]Mail Box 5151, Technical Institute of Physics and Chemistry, Chinese Academy of Science, Beijing 100101, People's Republic of China, and [b]College of Chemistry and Chemical Engineering, Yunnan Normal University, Kunming, People's Republic of China

Correspondence e-mail:
yumingming05@sohu.com

The title complex, $[Cu_2(C_{10}H_4N_4)(C_{41}H_{39}P_3)_2](BF_4)_2\cdot CH_2Cl_2$, was synthesized and characterized. Two copper(I) ions are bridged by 4,4′-di-4-pyridyldiazene (more commonly as 4,4′-azobipyridine). The discrete dinuclear cation contains two distorted tetrahedral copper(I) centers. Each Cu^I atom is coordinated by one 1,1,1-tris(diphenylphosphinomethyl)ethane molecule and one 4,4′-azobipyridine ligand. The complex sits on a center of symmetry; the solvent molecule is disordered across another center of symmetry. On irradiation of the copper(I) complex in dichloromethane at 365 nm, the *trans*/*cis* ratio of the complex is reversed.

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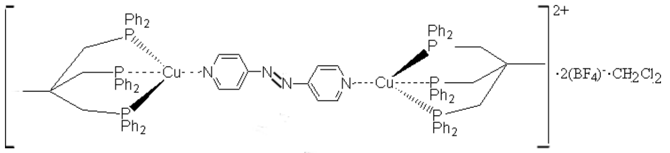
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
H-atom completeness 98%
Disorder in solvent or counterion
R factor = 0.048
wR factor = 0.146
Data-to-parameter ratio = 16.4

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

Comment

The construction of coordination polymers by linking transition metal centers with bidentate bridging ligands has recently received considerable attention (Batten & Robson, 1998; Blake *et al.*, 1998, 1999, 2000). The specific role of the bridging ligands is influenced by the acceptor and donor properties of the coordination sites, the length and rigidity of the spacers, presence or absence of conjugated bonds, and orientation of the substituents. A particularly promising class of ligands is represented by molecules containing two 4-pyridyl donor units interconnected by chains or groups of different types, such as 4,4′-bipyridine (4,4′-bipy), 4,4′-azobipyridine (4,4′-azbpy) or *trans*-1,2-bis(4-pyridyl)ethylene (bpe) (Carlucci *et al.*, 1997, 1999; Li *et al.*, 2001; Blake *et al.*, 1997, 1998; Zhang *et al.*, 2003; Yam *et al.*, 1998; Maji *et al.*, 2004; Barnett *et al.*, 2003; Abrahams *et al.*, 2003; Tanga *et al.*, 2003). Conjugated bridging ligands such as azo-containing compounds have aroused much interest because of their ability to stabilize metals in formally low oxidation states (Klein *et al.*, 1999). We report here the title complex, $[Cu_2(\mu\text{-}4,4'\text{-azpy})(tdpme)_2](BF_4)_2\cdot CH_2Cl_2$ [tdpme is 1,1,1-tris(diphenylphosphinomethyl)ethane and 4,4′-azbpy is 4,4′-azobipyridine], (I).



(I)

The complex comprises discrete, dimeric $[Cu_2(\mu\text{-}4,4'\text{-azbpy})(tdpme)_2]^{2+}$ cations [Cu···Cu = 13·21 (2) Å], BF_4^- anions and dichloromethane solvent molecules. The complex sits on a center of symmetry at the mid-point of the N—N bond. The dichloromethane molecule is disordered across a second center of symmetry. Each Cu atom has distorted

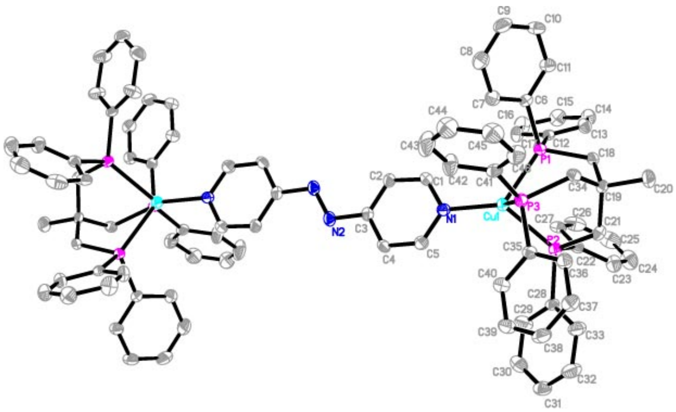


Figure 1
The molecular structure of the cation of (I). Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted.

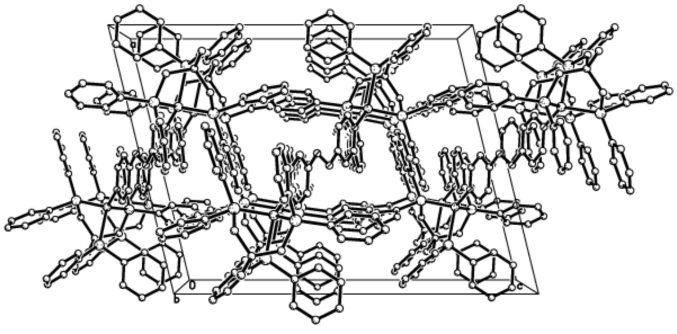


Figure 2
The unit cell structure of (I). H atoms, anions and solvent molecules have been omitted.

tetrahedral geometry [Cu1—N1 = 2.072 (4) Å, Cu1—P2 = 2.3145 (19) Å, Cu1—P3 = 2.330 (2) Å and Cu1—P1 = 2.337 (2) Å] and is coordinated by tdpme and a bridging 4,4′-azbpy (Table 1). The Cu—N bond lengths vary from 2.072 (4) to 2.337 (2) Å, the P—Cu—P angles from 91.80 (7) to 96.85 (6)° and the N—Cu—P angles from 118.74 (13) to 127.11 (13)°, indicating that the coordination geometry around the metal center is best described as pseudo-tetrahedral with two non-equivalent ligands.

Experimental

All reactions were performed under a nitrogen atmosphere. Solvents were distilled using standard techniques and saturated with dinitrogen before use. $[Cu(CH_3CN)_4]BF_4$ was prepared according to a published method (Kubas *et al.*, 1990), and 1,1,1-tris(diphenylphosphinomethyl)ethane (Acros, 99%) and 4-aminopyridine (Beijing, AR) were obtained commercially. All solvents were dried and distilled prior to use. $[Cu(CH_3CN)_4]BF_4$ (0.314 g, 0.1 mmol) was added to a solution of 1,1,1-tris(diphenylphosphinomethyl)ethane (0.625 g, 1 mmol) in dichloromethane (30 ml). The mixture was stirred under a nitrogen atmosphere at room temperature for 2 h. 4,4′–Azopyridine (0.092 g, 0.05 mmol) was added. Crystallization by slow diffusion of diethyl ether into a dichloromethane solution yielded brown crystals suitable for X-ray diffraction (yield: 80%). Analysis calculated: C 61.35, H 4.84, N 3.08%; found: C 61.30, H 4.83, N 3.02%. IR: 3433 (*m*), 3127 (*m*), 2933 (*w*), 1657 (*m*), 1615 (*m*), 1481 (*m*), 1435 (*s*), 1402 (*vs*), 1060 (*s*), 855 (*m*), 736 (*s*) 694 (*vs*), 513 (*vs*) cm^{-1}. The N═N azo stretch vibration (Beadle *et al.*, 1969; Grzeskowiak *et al.*, 1975) appears as a strong peak at 1430 cm^{-1}. The pyridyl C═C stretching vibration appears as a strong peak at 1610 cm^{-1} (Barandika *et al.*, 2000).

Crystal data

$[Cu_2(C_{10}H_4N_4)(C_{41}H_{39}P_3)_2](BF_4)_2\cdot CH_2Cl_2$
$M_r = 1819.09$
Monoclinic, $P2_1/c$
$a = 16.029\ (11)$ Å
$b = 12.985\ (9)$ Å
$c = 21.106\ (14)$ Å
$\beta = 103.768\ (12)^\circ$
$V = 4267\ (5)$ Å^3
$Z = 2$
$D_x = 1.416$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 933 reflections
$\theta = 3.4–23.2^\circ$
$\mu = 0.74$ mm^{-1}
$T = 293\ (2)$ K
Block, brown
0.22 × 0.20 × 0.16 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.834$, $T_{max} = 0.883$
23 889 measured reflections
8715 independent reflections
4513 reflections with $I > 2\sigma(I)$
$R_{int} = 0.100$
$\theta_{max} = 26.4^\circ$
$h = -18 \rightarrow 19$
$k = -14 \rightarrow 16$
$l = -26 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.146$
$S = 1.05$
8715 reflections
533 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0727P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.75$ e Å^{-3}
$\Delta\rho_{min} = -0.58$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	2.072 (4)	N2—N2^i	1.247 (8)
Cu1—P2	2.3145 (19)	N2—C3	1.442 (6)
Cu1—P3	2.330 (2)	C18—C19	1.542 (7)
Cu1—P1	2.337 (2)	C19—C20	1.536 (7)
P1—C18	1.836 (5)	C19—C34	1.546 (7)
P2—C21	1.853 (5)	C19—C21	1.554 (7)
P3—C34	1.838 (5)		
N1—Cu1—P3	121.46 (13)	P2—Cu1—P1	93.25 (6)
P2—Cu1—P3	91.80 (7)	P3—Cu1—P1	96.85 (6)
N1—Cu1—P1	118.74 (13)	N2^i—N2—C3	114.1 (5)
N2^i—N2—C3—C4	164.1 (6)	N2^i—N2—C3—C2	−16.9 (9)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

All H atoms were initially located in a difference Fourier map. The pyridyl and phenyl H atoms were then constrained to an ideal geometry, with C—H distances of 0.93 Å and $U_{iso}(H) = 1.5U_{eq}(C)$. The H atoms of the disordered dichloromethane could not be located in difference maps and were omitted from the refinement.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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