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catena-Poly[[[μ-di-4-pyridyldiazene-κ^2N^4:$N^{4'}$-bis[(triphenylphosphine-κP)copper(I)]]-μ-pyridine-2-carbaldehyde azine-κN^2,N:N',$N^{2'}$] bis(tetrafluoroborate)]

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.011 Å
Disorder in solvent or counterion
R factor = 0.067
wR factor = 0.210
Data-to-parameter ratio = 13.4

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

The title polymeric copper(I) complex, {[Cu$_2$(4,4′-azpy)(μ-paa)(C$_{18}$H$_{15}$P)$_2$](BF$_4$)$_2$}$_\infty$, [4,4′-azpy = di-4-pyridyldiazene (C$_{10}$H$_8$N$_4$) and paa = pyridine-2-carbaldehyde azine (C$_{12}$H$_{10}$N$_4$)] has been prepared and the crystal structure determined. The copper(I) centres adopt a distorted tetrahedral coordination geometry and are linked through binucleating azpy and paa ligands.

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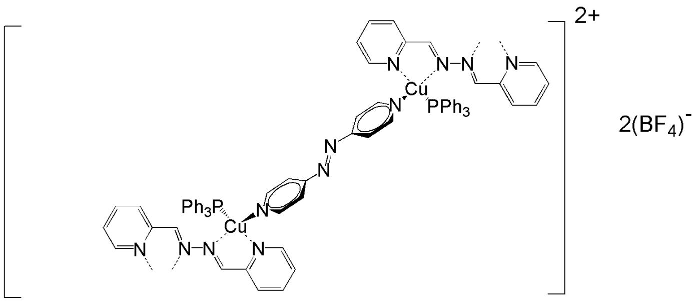
Comment

There has been great interest in the crystal engineering of coordinated frameworks, because of their potential applications as zeolite-like materials in molecular selection, ion exchange and catalysis, and their intriguing variety of architectures and topologies (Kitagawa *et al.*, 2004; KumarMaji *et al.*, 2004; Evans *et al.*, 1999; Zheng *et al.*, 2002). A number of extended infinite frameworks, such as linear, zigzag, diamondoid, grid, ladder and brick-wall frameworks, have been synthesized. These frameworks use ligands containing two 4-pyridyl donor units interconnected by chains or groups of different types, such as 4,4′-bipyridine (4,4′-bipy), di-4-pyridyldiazene (4,4′-azpy) or *trans*-1,2-bis(4-pyridyl)ethylene (bpe) (Lu *et al.*, 1997; Subramaian & Zaworortko, 1995; Withersby *et al.*, 1999; Zu *et al.*, 2003). Conjugated bridging ligands, such as azo-containing compounds, have also received great attention because of their ability to stabilize metals in formally low oxidation states (Frantz *et al.*, 2003; Klein *et al.*, 1999). In this report, we describe the synthesis and characterization of a polynuclear copper(I) complex with the general formula {[Cu$_2$(μ-4,4′-azpy)(μ-paa)(PPh$_3$)$_2$](BF$_4$)$_2$}$_\infty$ (paa = pyridine-2-carbaldehyde azine), (I). The structure of (I) is illustrated in Fig. 1, and selected bond distances and angles are given in Table 1.



(I)

The structure of (I) consists of one-dimensional staircase chains in the form of —(μ-azpy)Cu(PPh$_3$)(μ-paa)Cu(PPh$_3$)— cations with BF$_4^-$ as the counter-anion (Fig. 2). The P atom of PPh$_3$ occupies one coordination site, with a Cu—P bond

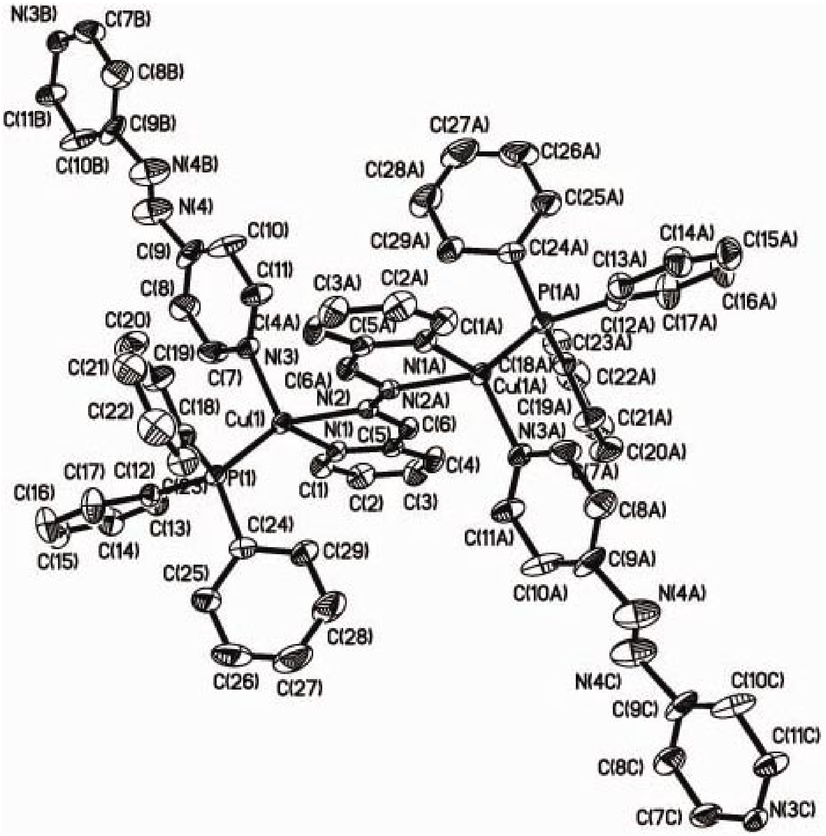


Figure 1

The dicationic repeat unit in the crystal structure of (I). Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (A) $1 - x$, $2 - y$, $1 - z$; (B) $2 - x$, $2 - y$, $-z$; (C) $x - 1$, y, $1 + z$.]

length of 2.196 (2) Å. The paa ligand, which is derived from hydrazine and contains a single N—N bond, provides a binucleating coordination mode to form two five-membered chelate rings with the Cu atoms, resulting in an S-frame configuration. The intermetallic Cu···Cu distance through the bridging paa ligand is 5.341 (7) Å. The copper sites are linked through pyridine N atoms from the azpy ligand. The pyridyl rings of the azpy molecules are not involved in π–π interactions. The Cu···Cu separation of 12.985 (8) Å can be compared with that in the paa-bridged Cu atoms. The coordination geometry of the Cu^{I} atom is distorted tetrahedral because of the restricted bite angle of the polydentate paa ligand (Table 1). The N—N bond length N2—N2^{i} (symmetry code as in Table 1) of 1.413 (8) Å can be formally defined as a single bond. The C—N bond lengths C6—N2 and C6^{i}—N2^{i} are equal [1.262 (7) Å] and are considered to have full double-bond character.

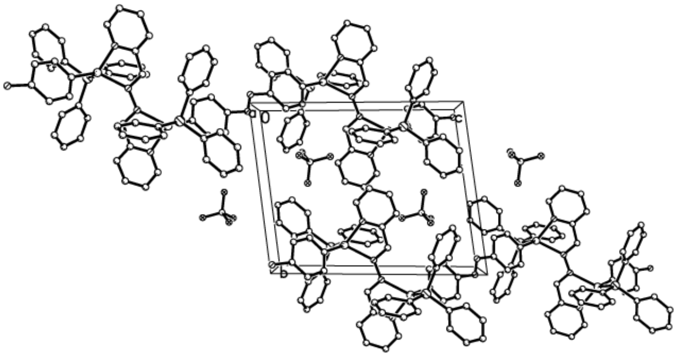


Figure 2

A perspective view of (I) along the *a* axis.

Experimental

All reactions were performed under a nitrogen atmosphere. Solvents were distilled using standard techniques and saturated with nitrogen before use. The ligands (paa and azpy) and the precursor complex [Cu(CH$_3$CN)$_4$]BF$_4$ were prepared and purified following literature procedures (Kubas *et al.*, 1990; Launay *et al.*, 1991; Baer & Macartney, 2000; Edwards *et al.*, 1998). For the synthesis of (I), a mixture of [Cu(MeCN)$_4$]BF$_4$ (77.8 mg, 0.247 mmol), 4,4′-azpy (27.0 mg, 0.124 mmol), paa (26.0 mg, 0.124 mmol) and PPh$_3$ (69.3 mg, 0.248 mmol) in dichloromethane (20 ml) was stirred overnight under a nitrogen atmosphere at room temperature. The resulting red solution was concentrated in vacuum and the crude product was precipitated by adding diethyl ether. The solid was filtered off and redissolved in a minimum of dichloromethane. Dark-red single crystals suitable for X-ray diffraction analysis were obtained from a dichloromethane solution of the complex by vapour diffusion with diethyl ether. Elemental analysis (%) calculated for $C_{58}H_{48}B_2Cu_2F_8N_8P_2$: C 57.11, H 3.97, N 9.19%; found: C 57.01, H 3.95, N 9.17%.

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Crystal data

$[Cu_2(C_{10}H_8N_4)(C_{12}H_{10}N_4)(C_{18}H_{15}P)_2](BF_4)_2$
$M_r = 1219.68$
Triclinic, $P\overline{1}$
$a = 10.262\ (9)$ Å
$b = 10.767\ (10)$ Å
$c = 13.437\ (12)$ Å
$\alpha = 81.790\ (14)^\circ$
$\beta = 82.515\ (13)^\circ$
$\gamma = 84.724\ (14)^\circ$
$V = 1453\ (2)$ Å^3
$Z = 1$
$D_x = 1.394$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 867 reflections
$\theta = 2.3$–22.5°
$\mu = 0.86$ mm^{-1}
$T = 293\ (2)$ K
Block, red
$0.20 \times 0.18 \times 0.14$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.794$, $T_{max} = 0.887$
7407 measured reflections
5090 independent reflections
3586 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$
$\theta_{max} = 25.0^\circ$
$h = -11 \rightarrow 12$
$k = -12 \rightarrow 8$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.210$
$S = 1.06$
5090 reflections
379 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1258P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.01$ e Å^{-3}
$\Delta\rho_{min} = -0.56$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N3	2.050 (4)	P1—C24	1.817 (5)
Cu1—N1	2.066 (4)	N2—C6	1.262 (7)
Cu1—N2	2.133 (4)	N2—N2^{i}	1.413 (8)
Cu1—P1	2.196 (2)	N4—N4^{ii}	1.099 (13)
P1—C12	1.802 (6)	N4—C9	1.505 (9)
P1—C18	1.811 (6)		
N3—Cu1—N1	102.84 (18)	C1—N1—Cu1	128.2 (4)
N3—Cu1—N2	111.93 (18)	C6—N2—N2^{i}	113.5 (5)
N1—Cu1—N2	78.27 (17)	C6—N2—Cu1	112.2 (3)
N3—Cu1—P1	113.53 (15)	N2^{i}—N2—Cu1	133.7 (4)
N1—Cu1—P1	128.80 (13)	N4^{ii}—N4—C9	107.0 (11)
N2—Cu1—P1	116.55 (12)	N1—C5—C6	115.4 (4)
C12—P1—C18	103.0 (3)	N2—C6—C5	119.5 (5)
C12—P1—C24	104.0 (3)	C11—N3—Cu1	122.2 (4)
C12—P1—Cu1	114.76 (18)	C7—N3—Cu1	119.1 (4)
C18—P1—Cu1	114.2 (2)	C10—C9—N4	129.7 (8)
C24—P1—Cu1	115.4 (2)	C8—C9—N4	110.8 (7)
C5—N1—Cu1	114.1 (3)		
N2^{i}—N2—C6—C5	−179.3 (5)	C4—C5—C6—N2	170.1 (5)
N1—C5—C6—N2	−8.6 (7)		

Symmetry codes: (i) $1 - x, 2 - y, 1 - z$; (ii) $2 - x, 2 - y, -z$.

All H atoms were positioned geometrically (C—H bond lengths fixed at 0.93 Å), assigned $U_{iso}(H) = 1.2U_{eq}(C)$ and refined as riding.

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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