### metal-organic papers

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#### **Key indicators**

Single-crystal X-ray study T = 292 K Mean  $\sigma$ (C–C) = 0.014 Å Disorder in solvent or counterion R factor = 0.066 wR factor = 0.216 Data-to-parameter ratio = 12.2

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

# catena-Poly[[[ $\mu$ -pyridine-2-carbaldehyde azine- $\kappa^4 N, N': N'', N'''$ -bis[(triphenylphosphine- $\kappa P$ )-copper(I)]]- $\mu$ -1,2-bis(4-pyridyl)ethene- $\kappa^2 N:N'$ ] bis(tetrafluoroborate)]

In the title complex, {[ $Cu_2(C_{12}H_{10}N_2)(C_{12}H_{10}N_4)(C_{18}H_{15}P)_2$ ]-(BF<sub>4</sub>)<sub>2</sub>}<sub>n</sub>, the cations form a linear chain, and are bridged by 1,2-bis(4-pyridyl)ethene and pyridine-2-carbaldehyde azine. Each Cu<sup>1</sup> atom is coordinated by one P atom of a PPh<sub>3</sub> ligand, two N atoms of a pyridine-2-carbaldehyde azine bridging ligand and one N atom of a bridging 1,2-bis(4-pyridyl)ethene ligand. There is a crystallographic centre of symmetry at the mid-point of the N–N bond.

#### Comment

Neutral 4-pyridyl ring ligands, such as 4,4-bipyridine (bpy), pyrazine or 1,2-bis(4-pyridyl)ethene, are excellent bridging ligands (Yaghi *et al.*, 1997). Yu *et al.* (2004) have reported a new linear chain bridged by 4,4'-azobispyridine and pyridine-2-carbaldehyde azine. We describe here the synthesis and structure of a new copper(I) compound, (I).



The crystal structure of (I) is depicted in Fig. 1 and the molecular stacking along the b axis is shown in Fig. 2. Selected bond lengths and angles are listed in Table 1. There is a crystallographic centre of symmetry at the mid-point of the N-N bond. The structure consists of one-dimensional cationic polymers [ $\mu$ -pyridine-2-carbaldehyde azine-bis-[(triphenylphosphine)copper(I)]]- $\mu$ -1,2-bis(4-pyridyl)ethene and free tetrafluoroborate anions. The Cu<sup>I</sup> atom is coordinated by one P atom of a PPh<sub>3</sub> ligand, two N atoms of the bridging pyridine-2-carbaldehyde azine ligand and one N atom of the bridging 1,2-bis(4-pyridyl)ethene ligand. The coordination geometry of the Cu<sup>I</sup> atom is distorted tetrahedral. The Cu-N3 bond length is similar to that in [Cu<sup>I</sup>(4cyanopyridine)<sub>2</sub>(SCN)]<sub>n</sub> [2.1038 (13) Å; Lin *et al.*, 2004]. The Cu...Cu distance in (I), bridged by 1,2-bis(4-pyridyl)ethene, is 13.325 (5) Å, and the Cu $\cdots$ Cu distance bridged by pyridine-2-carbaldehyde azine is 5.452 (5) Å.

#### **Experimental**

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Hydrazine (1 ml, 11 mmol) was added dropwise to a solution of pyridine-2-carboxaldehyde (2.2 ml, 22 mmol) dissolved in ethanol (15 ml). Two drops of formic acid were added and the mixture was stirred at room temperature for 24 h. The yellow solid that formed

Received 27 February 2006 Accepted 6 March 2006 was filtered off and washed several times with ethanol-ether (1:1) (yield 91%). [Cu(MeCN)<sub>4</sub>]BF<sub>4</sub> (62.9 mg 0.2 mmol) was added to a dichloromethane solution (15 ml) of pyridine-2-carbaldehyde azine (21.0 mg, 0.1 mmol) under a nitrogen atmosphere at room temperature. The mixture was stirred for 20 min to give a yellow solution. 1,2-Bis(4-pyridyl)ethene (18.2 mg 0.1 mmol) and PPh<sub>3</sub> (52.4 mg, 0.2 mmol) were added to this solution. The mixture was stirred for 2 d. The filtrate was kept in a diethyl ether atmosphere for two weeks, during which time yellow block-shaped crystals were formed. Chemical analysis found: C 59.07, H 4.05, N 7.03%; calculated for C<sub>30</sub>H<sub>25</sub>BCuF<sub>4</sub>N<sub>3</sub>P: C59.20, H 4.14, N 6.91%.

#### Crystal data

$[Cu_2(C_{12}H_{10}N_2)(C_{12}H_{10}N_4)-$	Z = 1
$(C_{18}H_{15}P)_2](BF_4)_2$	$D_x = 1.386 \text{ Mg m}^{-3}$
$M_r = 1217.70$	Mo $K\alpha$ radiation
Triclinic, $P\overline{1}$	Cell parameters from 777
a = 10.196 (5) Å	reflections
b = 10.710 (6) Å	$\theta = 3.2-23.8^{\circ}$
c = 13.590 (7) Å	$\mu = 0.85 \text{ mm}^{-1}$
$\alpha = 82.447 \ (12)^{\circ}$	T = 292 (3) K
$\beta = 84.181 \ (12)^{\circ}$	Block, yellow
$\gamma = 84.620 \ (13)^{\circ}$	$0.20 \times 0.18 \times 0.16 \text{ mm}$
$V = 1458.8 (14) \text{ Å}^3$	

#### Data collection

Bruker SMART CCD area-detector	4985 independent reflections
diffractometer	2554 reflections with $I > 2\sigma(I)$
$\varphi$ and $\omega$ scans	$R_{\rm int} = 0.068$
Absorption correction: multi-scan	$\theta_{\rm max} = 25.0^{\circ}$
(SADABS; Sheldrick, 1996)	$h = -11 \rightarrow 12$
$T_{\min} = 0.845, T_{\max} = 0.876$	$k = -12 \rightarrow 12$
7124 measured reflections	$l = -11 \rightarrow 16$

#### Refinement

Refinement on  $F^2$ 
$$\begin{split} R[F^2 > 2\sigma(F^2)] &= 0.066 \\ wR(F^2) &= 0.216 \end{split}$$
S = 0.964985 reflections 407 parameters

## H-atom parameters constrained

th  $I > 2\sigma(I)$ 

 $w = 1/[\sigma^2(F_o^2) + (0.1091P)^2]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\rm max} < 0.001$  $\Delta \rho_{\rm max} = 0.80 \ {\rm e} \ {\rm \AA}^{-3}$  $\Delta \rho_{\rm min} = -1.17 \text{ e} \text{ Å}^{-3}$ 

#### Table 1

Selected geometric parameters (Å, °).

Cu1-N3	2.024 (6)	Cu1-P1	2.182 (2)
Cu1-N1	2.052 (6)	N2-N2 <sup>i</sup>	1.396 (10)
Cu1-N2	2.118 (5)	C12-C12 <sup>ii</sup>	1.09 (2)
	104.0 (2)	N1 C 1 D1	100 10 (17)
N3-Cu1-N1	104.0 (2)	NI-CuI-PI	128.12 (17)
N3-Cu1-N2	112.4 (2)	$C6 - N2 - N2^{1}$	114.0 (6)
N1-Cu1-N2	78.7 (2)	N2 <sup>i</sup> -N2-Cu1	133.4 (5)
N3-Cu1-P1	112.28 (17)	C12 <sup>ii</sup> -C12-C9	135 (2)
N2 <sup>i</sup> -N2-C6-C5	-179.2 (6)	C10-C9-C12-C12 <sup>ii</sup>	-11(2)
C8-C9-C12-C12 <sup>ii</sup>	170.4 (19)		

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

All H atoms were positioned geometrically (C-H bond lengths fixed at 0.93 Å) and refined as riding, with  $U_{iso}(H) = 1.2U_{eq}(C)$ . The maximum electron-density peak was located 1.19 Å from atom Cu1.

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97; molecular graphics: XP in SHELXTL (Sheldrick, 1998); software used to prepare material for publication: XP and SHELXL97.



Figure 1

The molecular structure of the title compound, showing the atomnumbering scheme and displacement ellipsoids drawn at the 40% probability level. Free tetrafluoroborate anions are not shown. The symmetry code for the unlabelled atoms is (1 - x, 2 - y, 2 - z).



#### Figure 2

A view of the packing in the title compound, along the b axis.

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