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Di-μ_3-bromo-dibromotetrakis[μ-diphenyl(2-pyridyl)phosphine)]tetracopper(I) dichloromethane hexasolvate

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In the title compound, $[Cu_4Br_4(C_{17}H_{14}NP)_4]\cdot 6CH_2Cl_2$, the centrosymmetric Cu_4Br_2 group is in a slightly distorted plane, forming a shuttle-like structure. Each of the Cu^I ions is coordinated by two Br, N and P atoms, with metal–metal bonds between neighbouring Cu atoms.

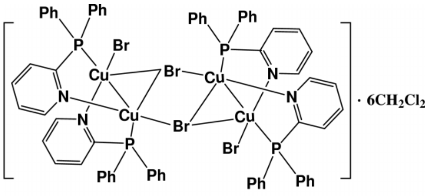
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.008 Å
R factor = 0.032
wR factor = 0.157
Data-to-parameter ratio = 17.5

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

Comment

The chemistry of transition metal clusters has attracted much attention owing to their relevance to certain biological catalysts and functional materials (Holm & Simhon, 1985; Holm, 1992; Du *et al.*, 1992). Transition metal complexes containing coordinated diphenyl(2-pyridyl)phosphine ($PyPPh_2$) have been studied for their structural chemistry. Much research has focused on the preparation of model compounds because of their catalytic and non-linear optical properties (Niu *et al.*, 2001). A rich structural diversity of $PyPPh_2$-containing Cu complexes has been revealed. The $PyPPh_2$ ligand can coordinate to Cu in different coordination fashions, such as monodentate and bidentate. We present here the structure of the title compound, (I).



(I)

The structure of the complex in (I) is centrosymmetric and the two independent Cu atoms are coordinated in different modes (Fig. 1). Atom Cu1 is coordinated by two μ_3-bridging Br atoms, and P and N atoms from $PyPPh_2$ ligands. Atom Cu2 is coordinated by a terminal Br atom, a μ_3-bridging Br atom, and P and N atoms from $PyPPh_2$ ligands. There are two different kinds of Br atoms: two are terminal and the other two are μ_3-bridging. Br1 coordinates to three Cu atoms in a μ_3-bridging bond mode, while atom Br2 is terminal. The bond lengths of Br1—Cu1, Br1—Cu2 and Br1—Cu1^i are 2.4645 (8), 2.5721 (8) and 2.8008 (8) Å, respectively (see Table 1 for symmetry code). The average Br—Cu bond length involving μ_3-Br is 2.6125 (8) Å, which is longer than that of the terminal Cu—Br bond [2.4754 (8) Å]. The $PyPPh_2$ ligand is bidentate and coordinates to two Cu atoms through its P and N atoms, forming a distorted Cu—Cu—P—C—N pentagon, with the angles ranging from 85.78 (4) to 124.7 (3)°. The average Cu—N bond length is 2.074 (4) Å, which is much shorter than the

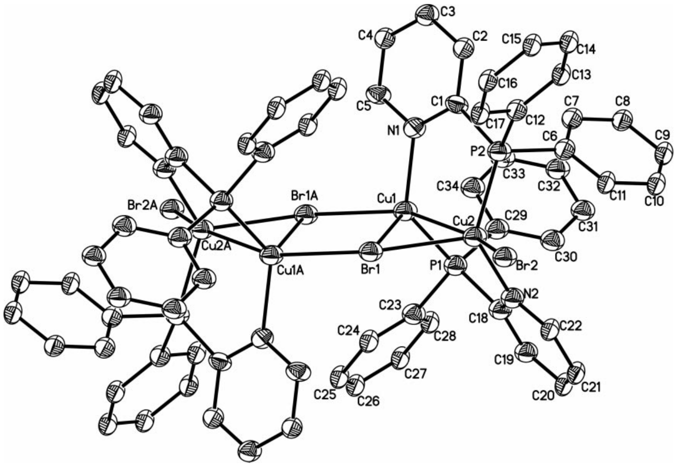


Figure 1
The structure of the complex in (I), shown with 30% probability displacement ellipsoids.

average Cu—P bond length [2.1920 (14) Å]. There are intermolecular C—H···Cl interactions (Fig. 2).

Experimental

The title compound, (I), was obtained by the reaction of CuBr (3 mmol, 0.430 g) with diphenyl(2-pyridyl)phosphine (3 mmol, 0.808 g) in CH_2Cl_2 solution (20 ml). The mixture was stirred for 8 h. The resulting solution was subsequently filtered to afford a light yellow filtrate. Light yellow crystals of (I) were obtained after several days by layering the filtrate with ^{i}PrOH. Elemental analysis, calculated for $Cu_4Br_4(PyPPh_2)_4 \cdot 6CH_2Cl_2$: C 41.60, H 3.21, N 2.62%; found: C 41.62, H 3.20, N 2.64%.

Crystal data

$[Cu_4Br_4(C_{17}H_{14}NP)_4] \cdot 6CH_2Cl_2$
$M_r = 2136.40$
Monoclinic, $P2_1/c$
$a = 13.818$ (1) Å
$b = 17.793$ (2) Å
$c = 19.292$ (2) Å
$\beta = 104.85$ (1)°
$V = 4584.8$ (8) Å^3
$Z = 2$
$D_x = 1.548$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3951 reflections
$\theta = 2.2$–20.2°
$\mu = 3.12$ mm^{-1}
$T = 293$ (2) K
Block, light yellow
0.3 × 0.2 × 0.2 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.476$, $T_{max} = 0.534$
23308 measured reflections
8072 independent reflections
6838 reflections with $I > 2\sigma(I)$
$R_{int} = 0.007$
$\theta_{max} = 25.0°$
$h = -16 \rightarrow 16$
$k = -21 \rightarrow 12$
$l = -22 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.157$
$S = 1.02$
8072 reflections
460 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.12P)^2 + 1.99P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.64$ e Å^{-3}
$\Delta\rho_{min} = -0.74$ e Å^{-3}

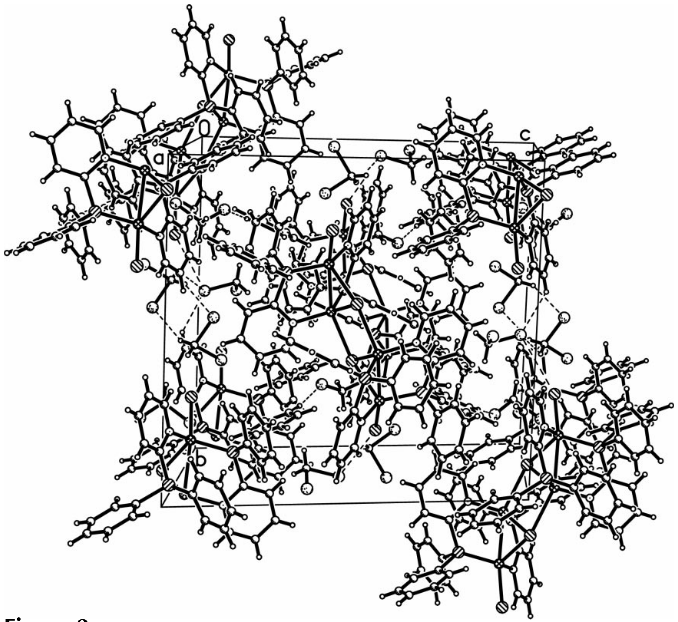


Figure 2
A packing diagram of (I), viewed down the *a* axis. Dashed lines indicate C—H···Cl interactions.

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	2.051 (4)	Cu2—N2	2.097 (4)
Cu1—P1	2.1699 (14)	Cu2—P2	2.2140 (14)
Cu1—Br1	2.4645 (8)	Cu2—Br2	2.4754 (8)
Cu1—Cu2	2.7556 (8)	Cu2—Br1	2.5721 (8)
Cu1—Br1^{i}	2.8008 (8)		
N1—Cu1—P1	124.21 (12)	P2—Cu2—Br2	105.64 (4)
N1—Cu1—Br1	114.65 (12)	N2—Cu2—Br1	109.64 (11)
P1—Cu1—Br1	114.42 (4)	P2—Cu2—Br1	113.87 (4)
N1—Cu1—Cu2	98.04 (10)	Br2—Cu2—Br1	105.08 (3)
P1—Cu1—Cu2	85.78 (4)	N2—Cu2—Cu1	91.48 (11)
Br1—Cu1—Cu2	58.72 (2)	P2—Cu2—Cu1	79.73 (4)
N1—Cu1—Br1^{i}	98.00 (10)	Br2—Cu2—Cu1	158.76 (3)
P1—Cu1—Br1^{i}	101.33 (4)	Br1—Cu2—Cu1	54.98 (2)
Br1—Cu1—Br1^{i}	96.40 (2)	Cu1—Br1—Cu2	66.30 (2)
Cu2—Cu1—Br1^{i}	154.45 (3)	Cu1—Br1—Cu1^{i}	83.60 (2)
N2—Cu2—P2	117.70 (12)	Cu2—Br1—Cu1^{i}	149.30 (3)
N2—Cu2—Br2	103.49 (11)		

Symmetry code: (i) $2 - x, 1 - y, 1 - z$.

All H atoms were positioned geometrically and refined with riding model constraints, with C—H distances set at 0.93 or 0.97 Å.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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