metal-organic papers

Bis[μ_2-phenylbis(2-pyridyl)phosphine]-$\kappa^3N,N':P;\kappa^3P:N,N'$-bis[chlorocopper(I)]

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The title dinuclear complex, [Cu$_2$Cl$_2$(C$_{16}$H$_{13}$N$_2$P)$_2$], possesses a crystallographically imposed inversion center. Two Cu atoms are connected by two bridging phenylbis(2-pyridyl)phosphine ligands. Each Cu atom adopts a distorted tetrahedral geometry, coordinated by one Cl atom [Cu—Cl = 2.3107 (6) Å], two N atoms [Cu—N = 2.065 (2) and 2.066 (2) Å] from one phenylbis(2-pyridyl)phosphine ligand and one P atom [Cu—P = 2.1757 (7) Å] from another ligand.

Comment

Phenylbis(2-pyridyl)phosphine (PhPPy$_2$) is an analog of di-2-pyridylamine that usually binds to metal atoms through two pyridyl groups. Such a feature is found in, for example, the mononuclear cobalt(II) dichloride adduct (Ehrlich *et al.*, 1984). However, in PhPPy$_2$, the P atom is also able to bind to transition metals with low oxidation states. This ligand can therefore coordinate to metals in different modes. In chloro-bis(triphenylphosphine)ruthenium(II) hexafluorophosphate (Shutte *et al.*, 1997), PhPPy$_2$ binds to the metal atom intra-molecularly, but intermolecularly in rhodium dichloride complexes (Galdecki *et al.*, 1999).

(I)
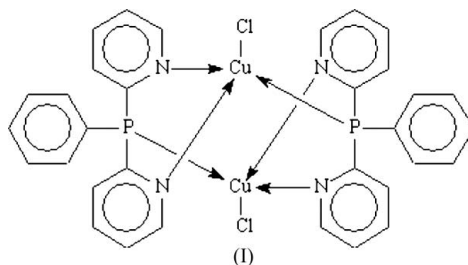
A direct reaction of [Cu$_2$(C$_{16}$H$_{13}$N$_2$P)$_2$(CH$_3$CN)$_2$](ClO$_4$)$_2$ [its crystal structure has recently been reported by Zhang *et al.* (2006)] with ammonium chloride led to the isolation of the title complex, (I), as yellow crystals, by substituting the labile acetonitrile molecules with Cl⁻. In the centrosymmetric dinuclear complex of (I), two Cu atoms are connected by two bridging PhPPy$_2$ ligands in a head-to-tail fashion. Each Cu atom is coordinated by one Cl and two N atoms from one PhPPy$_2$ ligand, and by one P atom from another PhPPy$_2$ ligand, in a distorted tetrahedral geometry (Table 1). The intramolecular Cu···Cu separation of 3.744 (1) Å in (I) indicates no interaction between copper centers.

Experimental

Solid [Cu$_2$(C$_{16}$H$_{13}$N$_2$P)$_2$(CH$_3$CN)$_2$](ClO$_4$)$_2$ (Zhang *et al.*, 2006) (0.0088 g, 0.0094 mmol) was dissolved in acetonitrile (2 ml), to which

a methanolic solution (1 ml) of ammonium chloride (0.0010 g, 0.0188 mmol) was added. The product, (I), crystallized as yellow crystals overnight in 80% yield.

Crystal data

$[Cu_2Cl_2(C_{16}H_{13}N_2P)_2]$
$M_r = 726.49$
Monoclinic, $P2_1/n$
$a = 9.305 (1)$ Å
$b = 10.857 (1)$ Å
$c = 15.746 (2)$ Å
$\beta = 93.033 (1)°$
$V = 1588.5 (3)$ Å^3

$Z = 2$
$D_x = 1.519$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.64$ mm^{-1}
$T = 293 (2)$ K
Block, yellow
$0.34 \times 0.14 \times 0.10$ mm

Data collection

Bruker APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
$T_{min} = 0.760$, $T_{max} = 0.849$

9241 measured reflections
3548 independent reflections
2901 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.094$
$S = 1.04$
3548 reflections
190 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0513P)^2 + 0.1517P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	2.065 (2)	Cu1—P1^i	2.1757 (7)
Cu1—N2	2.066 (2)	Cu1—Cl1	2.3107 (6)
N1—Cu1—N2	94.18 (7)	N2—Cu1—P1^i	115.99 (6)
N1—Cu1—P1^i	116.63 (6)	N2—Cu1—Cl1	103.04 (6)
N1—Cu1—Cl1	103.84 (6)	P1^i—Cu1—Cl1	119.42 (3)

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

H atoms were placed at idealized positions (C—H = 0.93 Å) and were included in the refinement in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine
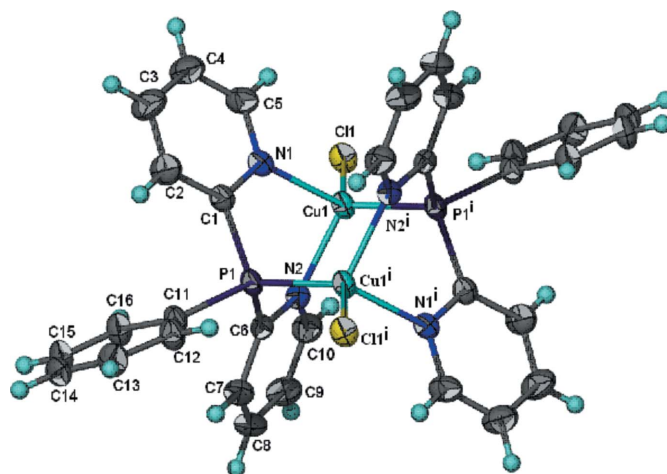

Figure 1
The molecular structure of (I), showing the atom-labeling scheme and displacement ellipsoids drawn at the 50% probability level [symmetry code: (i) $1 - x, 1 - y, 1 - z$].

structure: SHELXL97 (Sheldrick, 1997); molecular graphics: X-SEED (Barbour, 2001); software used to prepare material for publication: publCIF (Westrip, 2006).

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