

Chloro[(hydroxymethyl)diphenylphosphine- κP]-
(1,10-phenanthroline- $\kappa^2 N, N'$)copper(I)Qian-Yong Cao,^a Wen-Fu Fu^{a,b*}
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Key indicators

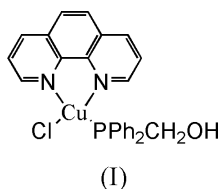
Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(C-C) = 0.005$ Å
Disorder in main residue
 R factor = 0.031
 wR factor = 0.072
Data-to-parameter ratio = 16.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, $[CuCl(C_{12}H_8N_2)(C_{13}H_{13}OP)]$, has a distorted tetrahedral coordination geometry at the copper(I) center, formed by the two N atoms from 1,10-phenanthroline, the P atom from the (hydroxymethyl)diphenylphosphine group and the Cl atom. Both $O-H \cdots Cl$ and $C-H \cdots Cl$ interactions help to define the crystal packing.

Comment

Transition metal complexes with functional group ligands have been studied in recent years owing to their ability for surface modification or anchoring to metal oxide materials, and the most attractive application is that of the ruthenium polypyridine complexes which were used in dye-sensitized solar cells based on nanocrystalline films of TiO_2 (Hagfeldt & Gratzel, 2000; Gillaizeau-Gauthier *et al.*, 2001).

Indeed, many kind of chemical bonds, based on silanes (Ford & Rodgers, 1994), amides (Fox *et al.*, 1980), ethers (Zou & Wrighton, 1990), acetylacetonates (Heimer *et al.*, 1996), carboxylates (Nazeeruddin *et al.*, 1993) and phosphonates (Pechy *et al.*, 1995) have been used to attach photoactive and redox-active molecular complexes to metal oxides. Though many examples have reported for ruthenium-polypyridine complexes, to our knowledge, copper(I) complexes with a functional group ligand are rare so far. Since copper(I) complexes also display interesting photoluminescent properties, and are cheap and environmentally friendly (Armaroli, 2001; Scaltrito *et al.*, 2000), it is essential to research their photophysical and photochemical properties when binding to inorganic materials. We report here an example of a mononuclear copper(I) complex, *viz.* chloro[(hydroxymethyl)diphenylphosphine](1,10-phenanthroline)copper(I), (I) (Fig. 1), with a hydroxyl functional group, which can serve as an anchoring group to immobilize the complex on a metal oxide surface.



One of the benzene rings in (I) is disordered over two sets of positions (C13–C18 and C13'–C18'). The copper(I) center adopts a distorted tetrahedral geometry, with two N atoms provided by the chelating 1,10-phenanthroline, one P atom from the (hydroxymethyl)diphenylphosphine group and one Cl atom. The two Cu–N distances [2.085 (2) and 2.086 (2) Å;

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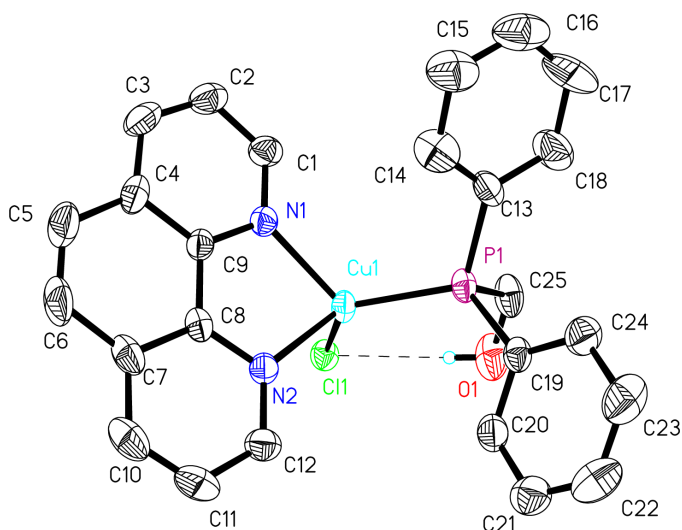


Figure 1
View of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level, and the minor disorder component of the C13–C18 benzene ring and all the H atoms, except the O–H species, have been omitted for clarity. The O–H...Cl interaction is indicated by a dashed line.

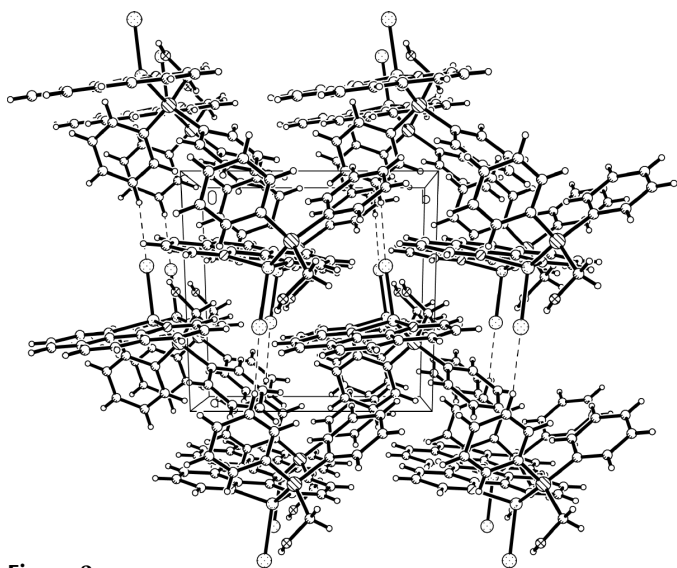


Figure 2
The packing in (I), with the C–H...Cl interactions indicated by dashed lines.

see Table 1] are almost the same, and they are comparable with the Cu–N bonds in $[(\text{CuCl})_2(o\text{-Phen})]_n$ [2.017 (7) and 2.100 (7) Å; Wang *et al.*, 2002]. The Cu–Cl and C–P distances are within the normal ranges for analogous complexes, such as $[(\text{PPh}_3)(\text{bpy})\text{Cu}X]$ (bpy = 2,2'-bipyridine; $X = \text{I}, \text{Br}, \text{Cl}$) (Barron *et al.*, 1988), and the bond angles about the Cu^{I} site vary from 80.49 (10) to 129.11 (7)°. The Cu^{I} atom is almost in the plane of the 1,10-phenanthroline ring, with a deviation of 0.090 (1) Å.

An intramolecular O1–H1A...Cl1 hydrogen bond exists in (I) (see Table 2). In addition, we find a non-classical C–H...Cl interaction (Braga *et al.*, 1998) between adjacent molecules, resulting in a one-dimensional supramolecular assembly, as depicted in Fig. 2.

Experimental

All the solvents were distilled before use and all the reactions were carried out under a nitrogen atmosphere. $\text{Ph}_2\text{PCH}_2\text{OH}$ was generated *in situ* by reaction of the air-stable phosphonium salt $[\text{Ph}_2\text{P}(\text{CH}_2\text{OH})_2]\text{Cl}$ with an equimolar amount of KOH in methanol, then the reaction solution was dropped into a mixture of equal amounts of $\text{Cu}(\text{CH}_3\text{CN})\text{BF}_4$ and 1,10-phenanthroline in methanol, and the resulting mixture was stirred at room temperature for 2 h. The solvent was removed and the residue was redissolved in an appropriate amount of dichloromethane. Orange crystals were obtained by vapor diffusion of diethyl ether into the dichloromethane solution.

Crystal data

$[\text{CuCl}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{C}_{13}\text{H}_{13}\text{OP})]$
 $M_r = 495.40$
 Monoclinic, $P2_1$
 $a = 10.8736$ (2) Å
 $b = 10.0773$ (2) Å
 $c = 11.7098$ (3) Å
 $\beta = 116.9420$ (9)°
 $V = 1143.86$ (4) Å³
 $Z = 2$

$D_x = 1.438$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 670 reflections
 $\theta = 2.6$ – 26.2°
 $\mu = 1.16$ mm⁻¹
 $T = 293$ (2) K
 Plate, orange
 $0.52 \times 0.35 \times 0.07$ mm

Data collection

Nonius KappaCCD diffractometer
 ω and φ scans
 Absorption correction: multi-scan
 (SORTAV; Blessing, 1995)
 $T_{\text{min}} = 0.795$, $T_{\text{max}} = 0.922$
 21658 measured reflections
 5022 independent reflections

4005 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$
 $\theta_{\text{max}} = 27.6^\circ$
 $h = -13 \rightarrow 13$
 $k = -13 \rightarrow 12$
 $l = -14 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.072$
 $S = 0.97$
 5022 reflections
 314 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0423P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.30$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.37$ e Å⁻³
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0102 (17)
 Absolute structure: Flack (1983),
 2207 Friedel pairs
 Flack parameter = 0.286 (10)

Table 1

Selected geometric parameters (Å, °).

Cu1–N1	2.085 (2)	Cu1–P1	2.1777 (7)
Cu1–N2	2.086 (2)	Cu1–Cl1	2.3463 (8)
N1–Cu1–N2	80.55 (9)	N1–Cu1–Cl1	109.26 (6)
N1–Cu1–P1	120.50 (6)	N2–Cu1–Cl1	101.97 (7)
N2–Cu1–P1	129.07 (6)	P1–Cu1–Cl1	111.13 (3)

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
O1–H1A...Cl1	0.82	2.38	3.181 (3)	165
C23–H23...Cl1 ⁱ	0.93	2.81	3.728 (5)	169

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

The two disorder components of the C13–C18 benzene ring were modelled as rigid hexagons, with C–C = 1.39 Å. The relative populations refined to 0.57 (3):0.43 (3) for C13–C18 and C13'–C18',

respectively. All the H atoms were located in difference Fourier maps. The C–H atoms were relocated in idealized positions and treated as riding (C–H = 0.97 Å for methylene and C–H = 0.93 Å for all other H atoms). The hydroxyl H atom was refined as riding in its as-found position. The refined Flack (1983) parameter indicates partial inversion twinning.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997), and *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1998); software used to prepare material for publication: *SHELXTL*.

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