

A centrosymmetric polymorph of chloridotris(triphenylphosphine- κP)-copper(I) at 150 K

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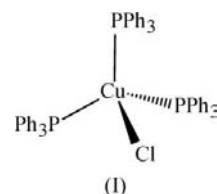
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This study characterizes a new polymorph of the title compound, $[\text{CuCl}(\text{C}_{18}\text{H}_{15}\text{P})_3]$, and analyses the influence of the extensive network of weak hydrogen-bonding interactions in the generation of this different crystal structure. The compound crystallizes in the centrosymmetric space group $C2/c$ with two crystallographically independent molecules per asymmetric unit, in contrast with the previously determined polymorph which crystallizes in the noncentrosymmetric space group $P3$ with three crystallographically independent molecules in the asymmetric unit, each with crystallographically imposed $C3$ symmetry [Gill, Mayerle, Welcker, Lewis, Ucko, Barton, Stowens & Lippard (1976). *Inorg. Chem.* **15**, 1155–1168]. The geometries of the two molecules of the title compound are very similar, with each having an approximately tetrahedral coordination around the central Cu atom and approximate C_s molecular symmetry. The molecules pack in chains parallel to the crystallographic b axis, connected by $\text{C}-\text{H}\cdots\text{Cl}$ and $\text{C}-\text{H}\cdots\pi(\text{phenyl})$ hydrogen bonds.

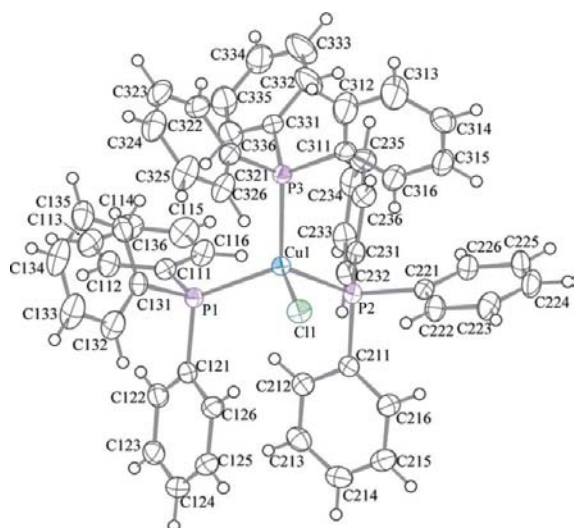
Comment

The phenomenon of polymorphism consists of the ability of a chemical substance to adopt more than one crystal structure. Different crystal structures of the same chemical material offer distinct physicochemical properties (Day *et al.*, 2006). The crystal structure of the title compound, (I), is an example of this. The compound has been determined in five different crystalline arrangements, either pure or in solvated forms. The first to be determined was the noncentrosymmetric polymorph (Gill *et al.*, 1976). In this structure, the compound is found in the trigonal space group $P3$ with three crystallographically independent molecules in the unit cell, each with crystallographically imposed $C3$ symmetry. The molecular packing is chiral, in which two of the three molecules possess S conformations and one an R conformation, using the 'steering wheel' convention (Albano *et al.*, 1971). The remaining four crystalline arrangements have been found as different solvates. Two, as acetone (Barron *et al.*, 1997) or acetonitrile (Kraüter & Neumüller, 1996) solvates, are found in the centrosymmetric space group $P\bar{1}$. The remaining two, both as tetrahydrofuran solvates, crystallize as two polymorphs, *viz.* a noncentrosymmetric form in $P6_3$ (Folting *et al.*, 1987) and a centrosymmetric form in $P2_1/c$ (Carlson *et al.*, 1996; Kraüter & Neumüller, 1996). This report presents the second known polymorph of the (pure) title compound.

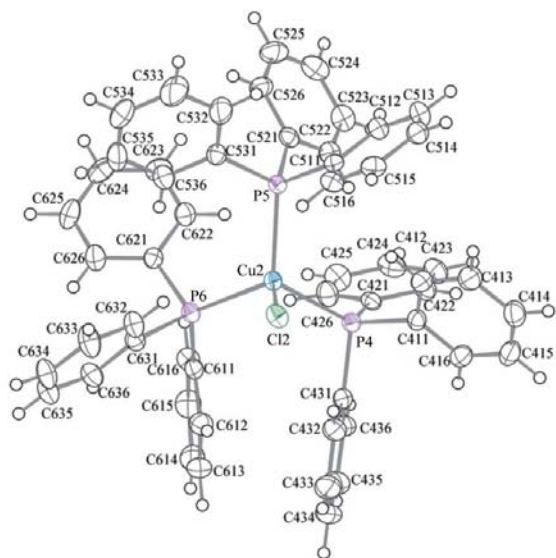


The asymmetric unit of (I) contains two complete independent molecules, denoted 1 and 2. The geometries of the two molecules are very similar; in both, the Cu atom has an approximately tetrahedral coordination geometry made up of three P atoms and one Cl atom. The average root-mean-square deviation of the atomic positions for the five central atoms for the superposition of molecules 1 and 2 (atom pairs Cu1/Cu2, Cl1/Cl2, P1/P6, P2/P4 and P3/P5) is 0.078 Å using the quaternion transformation method (Mackay, 1984) in *MOLFIT* (*PLATON*; Spek, 2003). The arrangement of the phenyl rings, however, is different between the molecules. The angles about the Cu atom show a distortion, with $\text{Cl}-\text{Cu}-\text{P}$ angles smaller than $108.86(2)^\circ$ and $\text{P}-\text{Cu}-\text{P}$ angles larger than $111.18(3)^\circ$, due to the 145° cone angle of PPh_3 (Tollman, 1977) (Table 1). Steric hindrance between the triphenylphosphine ligands is also shown by smaller than usual $\text{C}-\text{P}-\text{C}$ angles, with the smallest two [$\text{C}311-\text{P}3-\text{C}321 = 99.87(12)^\circ$ and $\text{C}611-\text{P}6-\text{C}631 = 99.69(11)^\circ$] being significantly different from the average for $\text{C}-\text{P}-\text{C}$ angles [$103.5(17)^\circ$ from 3638 observations in the Cambridge Structural Database (CSD, Version 5.28 of November, 2007; Allen, 2002)]. The distances around the Cu atoms are close to the averages found in the CSD for similar tetrahedral ClCuP_3 compounds (256 observations): $2.32(2)$ Å for $\text{Cu}-\text{Cl}$ and $2.31(2)$ Å for $\text{Cu}-\text{P}$ distances. The phenyl rings of the PPh_3 ligands are arranged in a symmetric fashion, according to the approximate C_s molecular symmetry. One phenyl ring of each triphenylphosphine ligand points in the opposite direction to the Cl atom; the $\text{Cl}-\text{Cu}-\text{P}-\text{C}$ torsion angles are about 180° , with the exception of $\text{Cl}2-\text{Cu}2-\text{P}6-\text{C}621$ (see the archived CIF). The other two phenyl rings cradle the Cl atom, with space to accommodate the neighbouring Cl atom in the crystal packing (see below).

Chains of each molecule of (I), connected by weak non-classical hydrogen bonds, are formed by crystallographic unit-cell translations along the b axis. The molecules pack in a head-to-tail fashion where the Cl atom 'head' fits into the spaces between the phenyl rings of the triphenylphosphine ligands of its own molecule and those of neighbouring molecules (Fig. 3). The interactions generate a network of weak



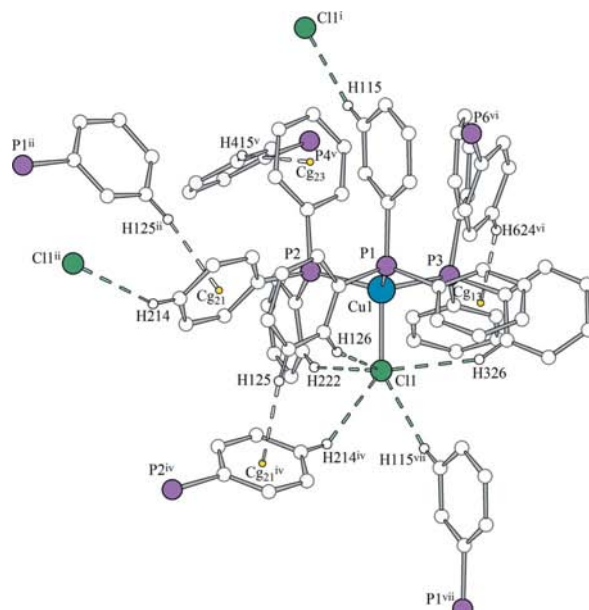
(a)



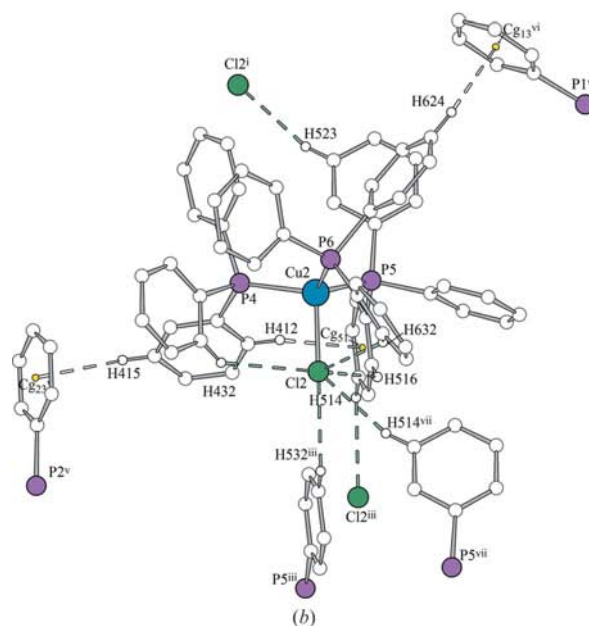
(b)

Figure 1
A view of the molecular structures of (a) molecule 1 and (b) molecule 2 of (I), showing the atom-labelling schemes. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

nonclassical hydrogen bonds between the molecules, making the packing arrangement interesting (Steiner & Desiraju, 1998; Desiraju & Steiner, 1999; Desiraju, 2002; Steiner, 2002; Brammer, 2004). The hydrogen bonding between the Cl atoms and the H atoms of neighbouring phenyl groups is shown as filled dashed lines in Fig. 2 and details are given in Table 2. Atoms Cl1 and Cl2 each participate in five C—H···*n* hydrogen bonds (*n* is a lone pair), with three intramolecular and two intermolecular interactions, with the Cl···H distances ranging from 2.61 to 2.93 Å. The sum of the radii is 2.95 Å (Bondi, 1964). Hydrogen bonds of the type C—H···*n*, where *n* is in this case the lone pair of the Cl atom, have been identified as influencing molecular packing (Balamurugan *et al.*, 2004). Hydrogen bonds involving the Cl—*M* group are fairly strong,



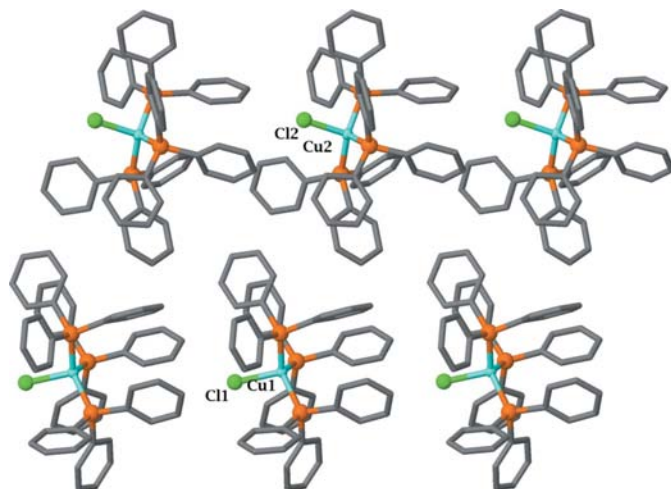
(a)



(b)

Figure 2
A close-up view of the hydrogen-bond interactions of (a) molecule 1 and (b) molecule 2 of (I). C—H···Cl interactions are indicated with filled dashed lines and C—H··· π interactions by unfilled dashed lines. Cg_{21} is the centroid of the C211–C216 ring, Cg_{51} of ring C511–C516, Cg_{23} of ring C231–C236 and Cg_{13} of ring C131–C136. [Symmetry codes: (i) $x, y + 1, z$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (v) $-x + 1, y, -z + \frac{1}{2}$; (vi) $-x + 1, -y + 1, -z$; (vii) $x, y - 1, z$.]

of the same order as those with Cl[−] interactions (Aullón *et al.*, 1998). Additionally, C—H··· π (C₆H₅) hydrogen bonds are observed, shown as unfilled dashed lines in Fig. 2, with distances to the ring centroid in the range 2.70–2.93 Å (Table 2). These weak bonds are of the order of 5 kJ mol^{−1} (Tsuzuki *et al.*, 2000). The directionality of the hydrogen bonds distinguishes them from simple van der Waals interactions (Steiner & Desiraju, 1998).


Figure 3

The head-to-tail packing of the molecules of (I) along the crystallographic *b* direction with the top row consisting entirely of molecules 2 and the bottom row of molecules 1.

Experimental

The title compound was synthesized by the dissolution of $[\text{CuCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ (0.05 g) in a mixture of methanol and acetone (1:1 *v/v*, 20 ml) followed by filtration. Colourless single crystals of (I) were obtained by evaporation of the solution at room temperature.

Crystal data

$[\text{CuCl}(\text{C}_{18}\text{H}_{15}\text{P})_3]$

$M_r = 885.80$

Monoclinic, $C2/c$

$a = 43.253$ (3) Å

$b = 9.9863$ (8) Å

$c = 44.354$ (3) Å

$\beta = 113.496$ (4)°

$V = 17570$ (2) Å³

$Z = 16$

Mo $K\alpha$ radiation

$\mu = 0.70$ mm⁻¹

$T = 150$ (2) K

$0.32 \times 0.16 \times 0.13$ mm

Data collection

Bruker X8 KappaAPEXII CCD area-detector diffractometer
Absorption correction: Gaussian [XPREP (Bruker, 2006)] was used to perform the Gaussian numeric absorption correction based on the face-indexed crystal size; SADABS (Bruker, 2006) was

used to perform further processing]

$T_{\min} = 0.844$, $T_{\max} = 0.927$

191602 measured reflections

25640 independent reflections

17309 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.075$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$

$wR(F^2) = 0.137$

$S = 1.02$

25640 reflections

1063 parameters

H-atom parameters constrained

$\Delta\rho_{\text{max}} = 1.27$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.72$ e Å⁻³

All H atoms were refined using a riding model, with $\text{C}-\text{H} = 0.93$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: APEX2, COSMO and BIS (Bruker, 2006); cell refinement: SAINT (Bruker, 2006); data reduction: SAINT, XPREP (Bruker, 2006) and SADABS (Bruker, 2006); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg, 2007); software used to prepare material for publication: SHELXL97.

Table 1

Selected geometric parameters (Å, °).

Cu1—Cl1	2.3070 (7)	Cu2—P4	2.3159 (7)
Cu1—P3	2.3208 (7)	Cu2—Cl2	2.3187 (6)
Cu1—P1	2.3228 (7)	Cu2—P6	2.3378 (7)
Cu1—P2	2.3274 (7)	Cu2—P5	2.3453 (7)
Cl1—Cu1—P3	101.44 (3)	P4—Cu2—Cl2	100.45 (3)
Cl1—Cu1—P1	104.25 (3)	P4—Cu2—P6	111.18 (3)
P3—Cu1—P1	113.78 (3)	Cl2—Cu2—P6	108.86 (2)
Cl1—Cu1—P2	104.05 (3)	P4—Cu2—P5	117.17 (2)
P3—Cu1—P2	116.41 (3)	Cl2—Cu2—P5	101.23 (2)
P1—Cu1—P2	114.54 (3)	P6—Cu2—P5	115.84 (3)

Table 2

Hydrogen-bond geometry (Å, °).

C_{g21} is the centroid of the C211–C216 ring, C_{g51} of ring C511–C516, C_{g23} of ring C231–C236 and C_{g13} of ring C131–C136.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C115—H115...Cl1 ⁱ	0.95	2.61	3.469 (3)	151
C214—H214...Cl1 ⁱⁱ	0.95	2.80	3.619 (3)	146
C126—H126...Cl1	0.95	2.79	3.667 (3)	154
C222—H222...Cl1	0.95	2.75	3.589 (3)	148
C326—H326...Cl1	0.95	2.80	3.659 (3)	151
C432—H432...Cl2	0.95	2.93	3.704 (3)	139
C514—H514...Cl2 ⁱⁱⁱ	0.95	2.91	3.619 (3)	132
C516—H516...Cl2	0.95	2.88	3.535 (3)	127
C523—H523...Cl2 ⁱ	0.95	2.84	3.764 (3)	164
C632—H632...Cl2	0.95	2.77	3.505 (4)	135
C125—H125... C_{g21} ^{iv}	0.95	2.80	3.668 (3)	152
C412—H412... C_{g51}	0.95	2.89	3.648 (3)	138
C415—H415... C_{g23} ^v	0.95	2.93	3.748 (3)	146
C624—H624... C_{g13} ^{vi}	0.95	2.70	3.579 (3)	154

Symmetry codes: (i) $x, y + 1, z$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (iv) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (v) $-x + 1, y, -z + \frac{1}{2}$; (vi) $-x + 1, -y + 1, -z$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3066). Services for accessing these data are described at the back of the journal.

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