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Key indicators

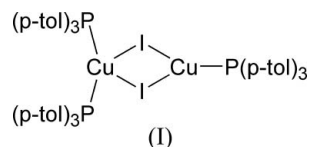
Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.007$ Å
 R factor = 0.045
 wR factor = 0.101
Data-to-parameter ratio = 20.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Di- μ -iodo-tris(tri-*p*-tolylphosphine)-1 κ P,2 κ^2 P-dicopper(I)

In the title compound, $[\text{Cu}_2\text{I}_2(\text{C}_{21}\text{H}_{21}\text{P})_3]$, one Cu^{I} atom is coordinated by one tri-*p*-tolylphosphine and two iodide ligands in a distorted trigonal-planar geometry, whereas the other Cu^{I} atom is coordinated by two phosphine and two iodide ligands in a distorted tetrahedral geometry.

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Comment

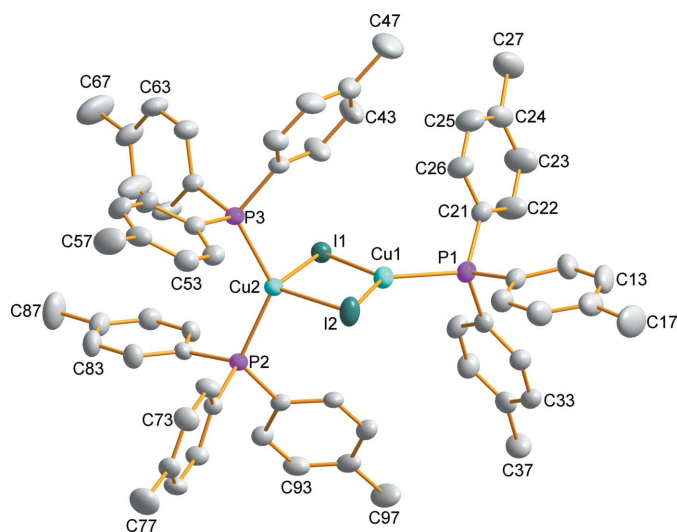
Copper(I)-phosphine complexes are generally prepared by two different synthetic routes: (i) by the reduction of the appropriate copper(II) salt with excess phosphine ligand and (ii) by direct reaction of a copper(I) halide with phosphine. A wide variety of coordination geometries and stoichiometries is known for complexes of general formula $[L_m(\text{Cu}X)_n]$ where L is a monodentate phosphine and X is generally a coordinating anion. Isolated $[L_m(\text{Cu}X)_n]$ complexes have been the subject of many investigations and their chemistry has been reviewed periodically (Murphy, 1993; Akrivos *et al.*, 1997; Hathaway, 1981, 1982, 1983; Lippard *et al.*, 1976; O'Brien, 1984).



Within the copper halide-triphenylphosphine system, a rare structural type containing a metal halide-ligand stoichiometry of 2:3 is known for all three halides (Gill *et al.*, 1976; Eller *et al.*, 1997). These complexes contain a Cu_2X_2 dimeric unit, with a four-coordinate copper atom with two terminal phosphines and a three-coordinate metal site with one attached phosphine ligand. Another example has been reported more recently for a CuI complex of $\text{P}(3\text{-MeC}_6\text{H}_4)_3$ (Akrivos *et al.*, 1993; Hossain *et al.*, 2005). The current structure, (I), is one of the few examples that contain this rare metal:phosphine stoichiometry.

In the structure of (I), one of the Cu^{I} atoms is coordinated by one phosphorus and two iodides in a trigonal-planar fashion (Fig. 1). The angles around the Cu^{I} atom deviate slightly from 120° . The other Cu^{I} atom is four-coordinate as it has two $\text{Cu}-\text{P}$ bonds and two $\text{Cu}-\text{I}$ bonds in a distorted tetrahedral environment. Here, also, the angles around the Cu^{I} atom are close to the ideal angles for tetrahedral coordination.

Monodentate phosphine complexes of copper(I) halides undergo extensive concentration-, temperature- and solvent-dependent dissociation in solution, and equilibria occur between complexes of the form $[L_m(\text{Cu}X)_n]$ with $m:n$


Figure 1

The molecular structure of (I), showing 30% probability displacement ellipsoids. H atoms have been omitted. For the C atoms, the first digit indicates ring number and the second digit indicates the position of the atom in the ring. Some labels have been omitted but all rings are numbered in a similar fashion.

stoichiometries of 3:1, 2:1, 1:1, 4:2, 3:2 and 2:2 (Lippard & Mayerle, 1972; Fife *et al.*, 1984). Owing to fast ligand exchange at the labile d^{10} Cu(I) centre and the dominant quadrupolar effects of this nucleus, solution ^{31}P NMR experiments often yield spectra that show broad signals at room temperature. Meaningful spectra are mostly unobtainable because of the dissociation of symmetrical (ideally tetrahedral) species in solution to species with lower symmetry and a dominant quadrupolar relaxation mechanism, thereby masking any useful NMR patterns that may exist.

Experimental

Copper(I) iodide (100 mg, 0.53 mmol) was added to a solution of tri-*p*-tolylphosphine (226 mg, 0.78 mmol) in pyridine (5 ml) and heated. The colourless solution was cooled and the title compound crystallized in quantitative yield on standing.

Crystal data

$[\text{Cu}_2\text{I}_2(\text{C}_{21}\text{H}_{21}\text{P})_3]$	$V = 2970.5$ (12) \AA^3
$M_r = 1293.92$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.447$ Mg m^{-3}
$a = 11.033$ (2) \AA	Mo $K\alpha$ radiation
$b = 13.757$ (3) \AA	$\mu = 1.87$ mm^{-1}
$c = 20.732$ (4) \AA	$T = 293$ (2) K
$\alpha = 94.81$ (3) $^\circ$	Cuboid, colorless
$\beta = 90.64$ (3) $^\circ$	$0.28 \times 0.26 \times 0.22$ mm
$\gamma = 108.54$ (3) $^\circ$	

Data collection

Bruker SMART CCD area-detector diffractometer	19806 measured reflections
ω and φ scans	13380 independent reflections
Absorption correction: multi-scan (SADABS; Bruker, 2004)	7750 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.604$, $T_{\max} = 0.663$	$R_{\text{int}} = 0.028$
	$\theta_{\text{max}} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.101$
 $S = 0.99$
 13380 reflections
 640 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.038P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.74$ e \AA^{-3}
 $\Delta\rho_{\text{min}} = -0.77$ e \AA^{-3}

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cu1—P1	2.2287 (16)	Cu2—P3	2.2754 (14)
Cu1—I2	2.5329 (8)	Cu2—I2	2.7332 (8)
Cu1—I1	2.5673 (8)	Cu2—I1	2.7618 (8)
Cu2—P2	2.2729 (13)		
P1—Cu1—I2	125.57 (4)	P3—Cu2—I1	105.20 (4)
P1—Cu1—I1	113.52 (4)	I2—Cu2—I1	107.56 (4)
I2—Cu1—I1	120.74 (4)	I2—Cu2—Cu1	53.52 (2)
P2—Cu2—P3	129.88 (5)	I1—Cu2—Cu1	54.04 (2)
P2—Cu2—I2	107.73 (4)	Cu1—I1—Cu2	65.41 (3)
P3—Cu2—I2	104.55 (4)	Cu1—I2—Cu2	66.28 (3)
P2—Cu2—I1	100.35 (4)		
P1—Cu1—I1—Cu2	176.31 (4)	P1—Cu1—I2—Cu2	−175.73 (5)
I2—Cu1—I1—Cu2	0.90 (2)	I1—Cu1—I2—Cu2	−0.90 (2)
P2—Cu2—I1—Cu1	−113.24 (5)	P2—Cu2—I2—Cu1	108.16 (5)
P3—Cu2—I1—Cu1	110.29 (5)	P3—Cu2—I2—Cu1	−110.73 (5)
I2—Cu2—I1—Cu1	−0.75 (4)	I1—Cu2—I2—Cu1	0.75 (4)

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D\text{—H}\cdots A$	$D\text{—H}$	$\text{H}\cdots A$	$D\cdots A$	$D\text{—H}\cdots A$
C16—H16 \cdots I2	0.93	3.06	3.971 (5)	167

Table 3

Comparative geometrical data (\AA , $^\circ$) for compounds of the general formula $[\text{Cu}_2\text{I}_2\{\text{PR}_3\}_3]$.

Phosphine	Cu1—P1	Cu2—P2	Cu2—P3	notes
PPh_3	2.219 (3)	2.259 (3)	2.267 (3)	(i)
$\text{P}(p\text{-tol})_3$	2.227 (3)	2.276 (3)	2.273 (3)	TW
$\text{P}(m\text{-tol})_3$	2.2298 (7)	2.2687 (7)	2.2737 (7)	(ii)

Notes: TW: this work; (i) Eller *et al.*, 1977; (ii) Hossain *et al.*, 2005.

The methyl and aromatic H atoms were placed in geometrically idealized positions ($\text{C—H} = 0.92\text{--}0.98$ \AA) and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for the aromatic H atoms. The Me groups show a high U_{eq} on the periphery of the molecule. Methyl H atoms were placed in idealized positions and the torsion angles refined to fit the electron density.

Data collection: SMART-NT (Bruker, 1999); cell refinement: SAINT-Plus (Bruker, 1999); data reduction: SAINT-Plus and XPREP (Bruker, 1999); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Brandenburg & Putz, 2005); software used to prepare material for publication: WinGX (Farrugia, 1999).

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References

- Akrivos, P. D., Hadjikakou, S. K., Karagiannidis, P., Mentzafos, D. & Terzis, A. (1993). *Inorg. Chim. Acta*, **206**, 163–168.
- Akrivos, P. D., Katsikis, H. J. & Koumoutsis, A. (1997). *Coord. Chem. Rev.* **167**, 95–204.
- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Brandenburg, K. & Putz, H. (2005). *DIAMOND*. Release 3.0c. Crystal Impact GbR, Bonn, Germany.
- Bruker (1999). *SAINT-Plus* (Version 6.02, including *XPREP*) and *SMART-NT* (Version 5.050). Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2004). *SADABS*. Version 2004/1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Eller, P. G., Kubas, G. J. & Ryan, R. R. (1977). *Inorg. Chem.* **16**, 2454–2462.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Fife, D. J., Moore, W. M. & Morse, K. W. (1984). *Inorg. Chem.* **23**, 1684–1691.
- Gill, J. T., Mayerle, J. J., Weleker, P. S., Lewis, D. F., Ucko, D. A., Barton, D. J., Stowens, D. & Lippard, S. J. (1976). *Inorg. Chem.* **15**, 1155–1168.
- Hathaway, B. J. (1981). *Coord. Chem. Rev.* **35**, 211–252.
- Hathaway, B. J. (1982). *Coord. Chem. Rev.* **41**, 423–487.
- Hathaway, B. J. (1983). *Coord. Chem. Rev.* **52**, 87–169.
- Hossain, G. M. G., Banu, A. & Seddigi, Z. S. (2005). *Acta Cryst.* **E61**, m2629–m2630.
- Lippard, S. J., Gill, J. T., Mayerle, J. J., Weleker, P. S., Lewis, D. F., Ucko, D. A., Bartort, D. J. & Stowen, D. (1976). *Inorg. Chem.* **15**, 1155–1168.
- Lippard, S. J. & Mayerle, J. J. (1972). *Inorg. Chem.* **11**, 753–759.
- Murphy, B. P. (1993). *Coord. Chem. Rev.* **124**, 63–105.
- O'Brien, P. (1984). *Coord. Chem. Rev.* **58**, 169–244.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.