

Iliana Medina, Joel T. Mague*
and Mark J. Fink*Department of Chemistry, Tulane University,
New Orleans, LA 70118, USACorrespondence e-mail: joelt@tulane.edu,
fink@tulane.edu

Key indicators

Single-crystal X-ray study
 $T = 100\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
Some non-H atoms missing
Disorder in solvent or counterion
 R factor = 0.027
 wR factor = 0.057
Data-to-parameter ratio = 28.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Tetra- μ_3 -iodo-tetrakis[(tri-*tert*-butylphosphine)-
copper(I)]

The title compound, $[\text{Cu}_4\text{I}_4(\text{C}_{12}\text{H}_{27}\text{P})_4]$, recovered from an attempt to prepare triisopropylsilylthiolato(tri-*tert*-butylphosphine)copper(I), is found to be tetrameric with a distorted heterocubane structure, one of the body diagonals of the cube being a crystallographic threefold rotation axis.

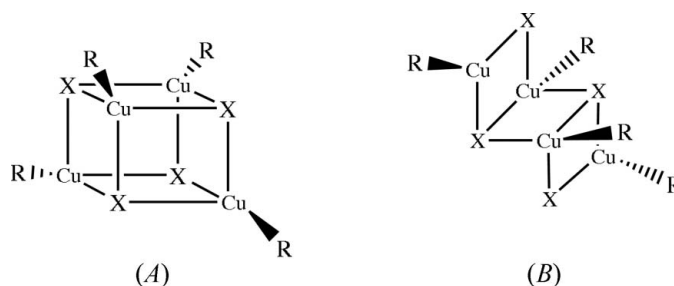
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Comment

Phosphine and arsine complexes of copper(I) halides $[(\text{MXL}_n)_m]$ ($X = \text{halogen}$ and $L = \text{phosphine}$ and arsine) display a rich coordination chemistry with a wide diversity of stoichiometries and geometries. R_3PCuX complexes are particularly useful as catalysts, as precursors to organocopper reagents (Taylor, 1994) and as starting materials for the preparation of complex heterometallic complexes (Albano *et al.*, 1995; Kudinov *et al.*, 1993). Monodentate phosphine and arsine complexes of copper(I) and silver(I) chlorides, bromides and iodides typically exist as tetrameric structures based on either cubane (*A*) or open 'step' (*B*) frameworks. Halides with these core structures often coexist in solution along with other oligomeric species. Steric repulsions appear to be a key factor governing the relative stabilities of the two core structures, with bulky phosphines and halogens favoring the 'open' structures *B* (Teo & Calabrese, 1976*a*, 1976*b*). Tri-*t*-butylphosphine copper(I) chlorides, bromides and iodides have been previously reported, but only the crystal structure of the bromide has been determined (Goel & Beauchamp, 1983). This was found to have a distorted heterocubane structure. The chloride and iodide complexes were also proposed to have heterocubane structures on the basis of their far-IR and Raman spectra. The X-ray structure of the title compound, ${}^t\text{Bu}_3\text{PCuI}$, (**I**), confirms this spectroscopic prediction of a heterocubane structure.



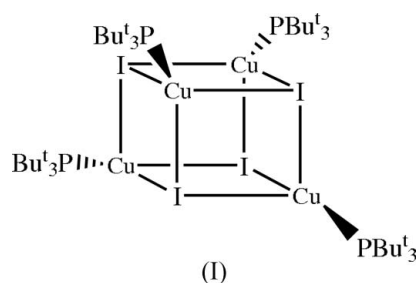


Fig. 1 gives a perspective view of (I), showing the distorted cubane Cu_4I_4 framework. The molecule has crystallographically imposed threefold symmetry with the threefold axis passing through I1 and the Cu2–P2 bond. Important bond lengths and angles are in Table 1, and a comparison of metrical parameters with related structures is given in Table 2. The cubane structure is significantly distorted, the mean Cu–I–Cu and I–Cu–I bond angles being $97.99(1)$ and $81.40(1)^\circ$, respectively. The distortion is probably the result of the extreme bulk of the tri-*tert*-butylphosphine ligand.

Experimental

${}^t\text{Bu}_3\text{PCuI}$ was synthesized by the published procedure (Goel & Beauchamp, 1983). X-ray quality crystals of ${}^t\text{Bu}_3\text{PCuI}$ were recovered from the attempted reaction of ${}^t\text{Bu}_3\text{PCuI}$ with $(\text{THF})_2\text{LiSSi}({}^t\text{Pr})_3$, in which a suspension of ${}^t\text{Bu}_3\text{PCuI}$ in benzene was reacted with an equimolar quantity of $(\text{THF})_2\text{LiSSi}({}^t\text{Pr})_3$ at low temperature. The solution turned colorless within minutes, and a white precipitate formed after 1 h. Filtration and recrystallization from benzene/pentane (1:1) afforded colorless crystals which proved to be ${}^t\text{Bu}_3\text{PCuI}$.

Crystal data

$[\text{Cu}_4\text{I}_4(\text{C}_{12}\text{H}_{27}\text{P})_4]$	Mo $K\alpha$ radiation
$M_r = 1571.03$	Cell parameters from 9205 reflections
Trigonal, $R\bar{3}$	$\theta = 2.4\text{--}28.2^\circ$
$a = 13.878(1) \text{ \AA}$	$\mu = 3.22 \text{ mm}^{-1}$
$c = 60.239(7) \text{ \AA}$	$T = 100(2) \text{ K}$
$V = 10047.7(16) \text{ \AA}^3$	Block, colorless
$Z = 6$	$D_x = 1.558 \text{ Mg m}^{-3}$
	$0.13 \times 0.09 \times 0.09 \text{ mm}$

Data collection

Bruker SMART APEX CCD area-detector diffractometer	5477 independent reflections
φ and ω scans	4891 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2002)	$R_{\text{int}} = 0.028$
$T_{\text{min}} = 0.624$, $T_{\text{max}} = 0.750$	$\theta_{\text{max}} = 28.3^\circ$
30297 measured reflections	$h = -18 \rightarrow 18$
	$k = -18 \rightarrow 17$
	$l = -79 \rightarrow 78$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0186P)^2 + 41.1166P]$
$R[F^2 > 2\sigma(F^2)] = 0.027$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.057$	$(\Delta/\sigma)_{\text{max}} = 0.003$
$S = 1.11$	$\Delta\rho_{\text{max}} = 0.77 \text{ e \AA}^{-3}$
5477 reflections	$\Delta\rho_{\text{min}} = -0.42 \text{ e \AA}^{-3}$
193 parameters	
H-atom parameters constrained	

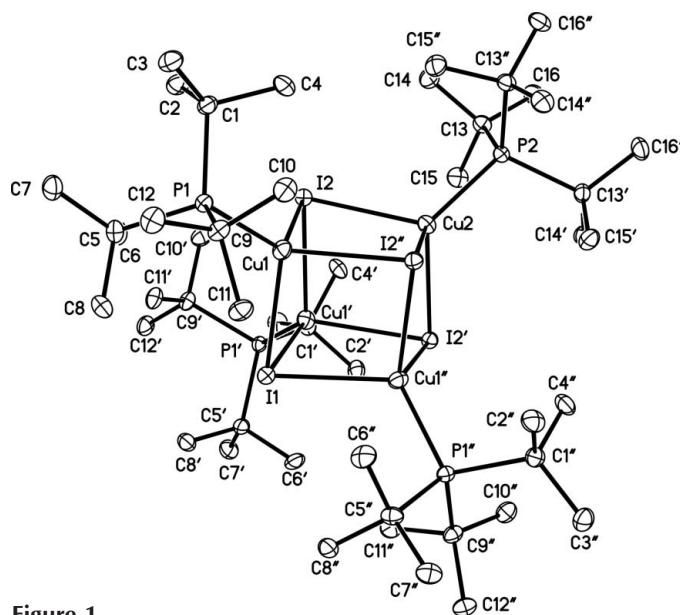


Figure 1

A perspective view of (I). Displacement ellipsoids have been drawn at the 50% probability level and H atoms have been omitted for clarity. [Symmetry codes: (') $1 - x + y, 1 - x, z$; (')' $1 - y, x - y, z$.]

Table 1

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

I1–Cu1	2.7300 (4)	Cu1–P1	2.2522 (7)
I2–Cu1	2.7204 (4)	Cu1–I2 ⁱ	2.7405 (4)
I2–Cu2	2.7273 (3)	Cu2–P2	2.251 (1)
Cu1 ⁱ –I1–Cu1	81.62 (1)	I2–Cu1–I1	98.03 (1)
Cu1–I2–Cu2	81.36 (1)	I2–Cu1–I2 ⁱ	98.13 (1)
Cu1–I2–Cu1 ⁱⁱ	81.61 (1)	I1–Cu1–I2 ⁱ	97.54 (1)
Cu2–I2–Cu1 ⁱⁱ	81.00 (1)	I2–Cu2–I2 ⁱⁱ	98.28 (1)

Symmetry codes: (i) $-x + y + 1, -x + 1, z$; (ii) $-y + 1, x - y, z$.

Table 2

Comparison of metrical parameters (\AA , $^\circ$) for $R_3\text{PMX}$ cubanes.

Compound	$M-X$	$M-P$	$X-M-X$	$X-M-P$	$M-X-M$
$[\text{Et}_3\text{PCu}]_4$ ^a	2.684 (1)	2.254 (3)	109.38 (4)	109.56 (8)	66.10 (4)
$[\text{Ph}_3\text{PCuCl}]_4$ ^b	2.4441 (8)	2.192 (2)	94.09 (2)	122.02 (3)	85.16 (2)
$[{}^t\text{Bu}_3\text{PCuBr}]_4$ ^c	2.5930 (6)	2.228 (3)	95.29 (2)	121.42 (4)	84.45 (2)
$[{}^t\text{Bu}_3\text{PCuI}]_4$ ^d	2.7297 (2)	2.2519 (7)	98.090 (4)	119.30 (1)	81.472 (4)
$[\text{Et}_3\text{PAGl}]_4$ ^e	2.9189 (6)	2.438 (2)	109.01 (1)	109.93 (2)	66.68 (1)
$[\text{Ph}_3\text{PAGCl}]_4$ ^f	2.653 (1)	2.382 (2)	92.72 (3)	122.35 (4)	86.48 (3)

References: (a) Churchill & Kalra (1974b); (b) Churchill & Kalra (1974a); (c) Goel & Beauchamp (1983); (d) this work; (e) Teo & Calabrese (1976a); (f) Churchill & DeBoer (1975).

H atoms were placed in calculated positions ($\text{C-H} = 0.98 \text{ \AA}$) and included as riding atoms, with $U_{\text{iso}}(\text{H})$ values of $1.5U_{\text{eq}}$ of the attached C atoms. A region of electron density attributable to an unidentified solvent molecule severely disordered about the threefold axis was removed with the *SQUEEZE* option of the *PLATON* package (Spek, 2003).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 2002); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXL97*.

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