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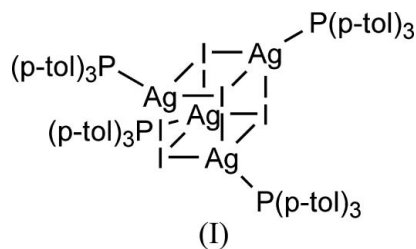
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Key indicators

Single-crystal X-ray study
 $T = 100\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.017
 wR factor = 0.067
Data-to-parameter ratio = 22.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Tetra- μ_3 -iodo-tetrakis[(tri-*p*-tolylphosphine- κP)-silver(I)]The title compound $[\text{Ag}_4\text{I}_4(\text{C}_{21}\text{H}_{21}\text{P})_4]$, crystallizes on a centre of symmetry. Each Ag atom is surrounded by one phosphine ligand and three iodide anions, forming a distorted tetrahedral configuration. The Ag–P distance is 2.4666 (7) Å and the Ag–I distances are 2.7972 (6), 2.8322 (10) and 3.1956 (6) Å.Received 28 July 2006
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Comment

Tertiary phosphine complexes of silver(I) of the type $[\text{AgXL}_n]$ (L = tertiary phosphine; $n = 1-4$; X = coordinating or non-coordinating anion) were first prepared by Mann *et al.* (1937). These coordination complexes of silver(I) salts display a rich diversity of structural types. The interplay of parameters such as the geometrical flexibility of silver(I), bite angle, electronic properties of the phosphine and the coordination mode of the supporting ligands often renders predictions concerning the structural properties of silver–phosphine complexes, both in solution and in the solid state, difficult.For equimolar stoichiometry ($L:\text{Ag} = 1$), both the tetranuclear cubane and step structures have been characterized. Noting the difference, it has been argued that control of the isomeric form may be determined by the relative stereochemical parameters of metal, halide and ligand (Teo & Calabrese, 1976*a,b*). More sterically demanding species were supposed to relieve strain by forming the step structure rather than the cubane geometry.However, the isolation and characterization of cubane $[\text{AgIPPh}_3]_4$ (Teo & Calabrese, 1975; Teo & Calabrese, 1976*a*) from $\text{CHCl}_3/\text{Et}_2\text{O}$ and the step analogue from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (Teo & Calabrese, 1976*a*; Bowmaker *et al.*, 1997), as well as the isolation of the sterically unfavoured cubanes $[\text{AgIPCy}_3]_4$ (Cy = cyclohexyl) (Bowmaker *et al.*, 1996), $[\text{CuIPPh}_3]_4$ (Dyason *et al.*, 1985) and $[\text{CuBrP}^t\text{Bu}_3]_4$ (Goel & Beauchamp, 1983) complexes, demonstrate the fact that the nature of the determining factors are not clearly understood.

We set out to identify which factors determine whether a cubane or step tetrameric structure is formed. As part of this research we report the structure of the centrosymmetric

[AgI{P(C₇H₇)₃}]₄, (I), as another example of the tetrameric cubane structure type.

The Ag—P bond length for the iodide cubane tetramer is 2.4666 (7) Å and lies in the same range as that for other cubane tetramers (Table 2). Similarly, Ag—I lies within the range typical for this type of complex (Table 2). In addition, all bond angles in (I) are comparable with previously reported angles for cubane type complexes.

It is interesting to note that the Ag—I bond distances are different for the three iodides around the silver. Earlier, dimers with different Ag—X bond lengths were described in terms of partial separation of the dimer into monomers (Bowmaker *et al.*, 1996). Similar distortions in the cubane type structure of [AgXPPH₃]₄ were, however, ascribed to steric interactions between the ligands (Teo & Calabrese, 1976a).

Experimental

Silver iodide (0.115 g, 0.49 mmol) and tri-*p*-tolylphosphine (0.15 g, 0.49 mmol) were dissolved in hot pyridine (10 ml) to give a clear solution. The solution was filtered through a pad of celite. Slow evaporation of the solvent provided, in quantitative yield, crystals of the title compound suitable for X-ray analysis.

Crystal data

[Ag ₄ I ₄ (C ₂₁ H ₂₁ P) ₄]	$D_x = 1.799 \text{ Mg m}^{-3}$
$M_r = 2156.47$	Mo $K\alpha$ radiation
Tetragonal, $I4_1/a$	$\mu = 2.64 \text{ mm}^{-1}$
$a = 23.986 (5) \text{ \AA}$	$T = 100 (2) \text{ K}$
$c = 13.842 (5) \text{ \AA}$	Block, colourless
$V = 7964 (4) \text{ \AA}^3$	$0.39 \times 0.17 \times 0.16 \text{ mm}$
$Z = 4$	

Data collection

Bruker X8 APEX-II 4K Kappa CCD diffractometer	35598 measured reflections
ω and φ scans	4955 independent reflections
Absorption correction: multi-scan (SADABS; Bruker, 2004)	4724 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.413$, $T_{\max} = 0.657$	$R_{\text{int}} = 0.02$
	$\theta_{\text{max}} = 28.3^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0352P)^2 + 4.0222P]$
$R[F^2 > 2\sigma(F^2)] = 0.017$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.067$	$(\Delta/\sigma)_{\text{max}} = 0.01$
$S = 1.42$	$\Delta\rho_{\text{max}} = 0.82 \text{ e \AA}^{-3}$
4955 reflections	$\Delta\rho_{\text{min}} = -1.56 \text{ e \AA}^{-3}$
220 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Ag—P	2.4666 (7)	P—C31	1.815 (2)
Ag—I	2.7972 (6)	P—C11	1.820 (2)
Ag—I ⁱ	2.8322 (10)	P—C21	1.822 (2)
Ag—I ⁱⁱ	3.1956 (6)		
P—Ag—I	121.20 (2)	I ⁱ —Ag—I ⁱⁱⁱ	107.889 (8)
P—Ag—I ⁱ	110.57 (2)	Ag—I—Ag ⁱⁱⁱ	66.891 (8)
I—Ag—I ⁱ	120.109 (7)	Ag—I—Ag ⁱⁱ	71.658 (7)
P—Ag—I ⁱⁱⁱ	93.793 (15)	Ag ⁱⁱⁱ —I—Ag ⁱⁱ	61.610 (6)
I—Ag—I ⁱⁱ	97.111 (8)		

Symmetry codes: (i) $-y + \frac{3}{4}, x - \frac{3}{4}, -z + \frac{9}{4}$; (ii) $-x + 2, -y + \frac{1}{2}, z$; (iii) $y + \frac{3}{4}, -x + \frac{5}{4}, -z + \frac{9}{4}$.

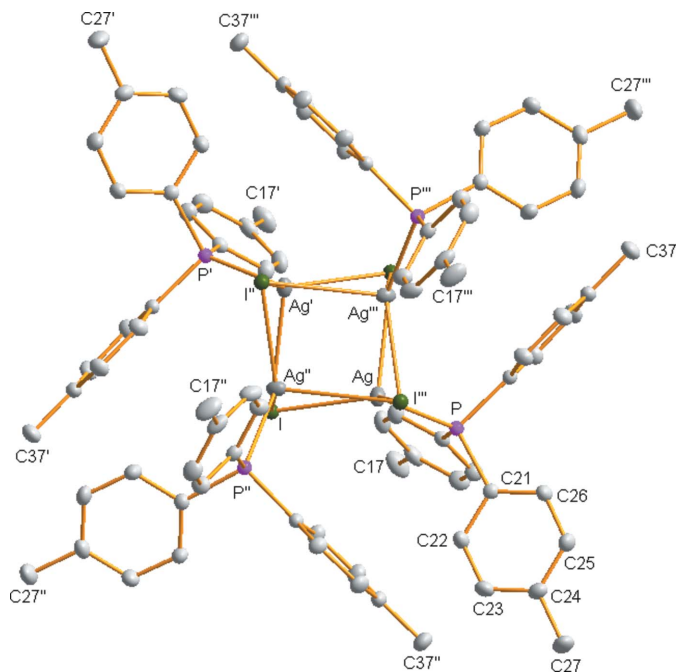


Figure 1

The structure of (I), showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity. For the C atoms, the first digit indicates the ring number and the second digit indicates the position of the atom in the ring. [Symmetry codes: (i) $2 - x, \frac{1}{2} - y, z$; (ii) $\frac{5}{4} - x, \frac{3}{4} + y, \frac{9}{4} - z$; (iii) $x - \frac{3}{4}, \frac{5}{4} - y, \frac{9}{4} - z$.]

Table 2

Comparative geometrical data (Å, °) for compounds of the general formula [AgI{PR₃}]₄.

Complex	Ag—P	Ag—X	P—Ag—X	X—Ag—X	Ag—X—Ag	Ref
(I)	2.4666 (7)	2.941 (1)	108.52 (1)	108.36 (1)	66.71 (1)	TW
(II)	2.438 (2)	2.918 (1)	109.9 (1)	109.0 (9)	66.7 (4)	<i>a</i>
(III)	2.43 (1)	2.90 (3)	114 (3)	104.0 (1)	73.8 (1)	<i>b</i>
(IV)	2.458 (3)	2.91 (8)	114 (6)	104 (6)	73 (5)	<i>c</i>
(V)	2.45 (2)	2.93 (9)	116 (1)	102 (7)	76 (5)	<i>d</i>

Notes: all values are average values; TW: this work; (II) [AgI(PEt₃)₄]; (III) [AgI(PPh₂Bu)₄]; (IV) [AgI(PPh₃)₄]; (V) [AgI(PCy₃)₄]. References: (*a*) Churchill & DeBoer (1975); (*b*) Bowen *et al.* (1994); (*c*) Teo & Calabrese (1976b); (*d*) Bowmaker *et al.* (1996).

Aromatic and methyl H atoms were placed in geometrically idealized positions (C—H = 0.97–0.98 Å) and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic and $1.5U_{\text{eq}}(\text{C})$ for methyl H atoms. Methyl H atoms were placed in idealized positions and the torsion angles refined to fit the electron density. The deepest residual electron-density hole is located 0.07 Å from the Ag atom.

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT-Plus (Bruker, 2004); data reduction: SAINT-Plus and XPREP (Bruker, 2004); 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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