

Di- $\mu$ -iodo-bis[pyridine(tri-*p*-tolylphosphine)silver(I)]

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## Key indicators

Single-crystal X-ray study

 $T = 298\text{ K}$ Mean  $\sigma(\text{C}-\text{C}) = 0.007\text{ \AA}$ 

Disorder in main residue

 $R$  factor = 0.030 $wR$  factor = 0.078

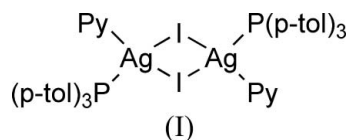
Data-to-parameter ratio = 14.9

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound,  $[\text{Ag}_2\text{I}_2(\text{C}_5\text{H}_5\text{N})_2(\text{C}_{21}\text{H}_{21}\text{P})_2]$ , has  $C_i$  molecular symmetry. Each Ag atom is surrounded by a phosphine ligand, a pyridine ligand and two iodide anions in a distorted tetrahedral coordination. The Ag $\cdots$ Ag separation in the binuclear species is 3.1130 (18) Å. The Ag–P distance is 2.4489 (12) Å, the Ag–N distance is 2.392 (3) Å, and the Ag–I distances are 2.8402 (14) and 2.8644 (8) Å.

## Comment

For silver, although the parent  $[\text{Ag}(\text{py})_4]^+$  and  $[\text{Ag}L_4]^+$  ( $L =$  phosphine) arrays have been structurally characterized, there are only a few accounts of mixed-base species  $[\text{Ag}(\text{py})_m(L)_{4-m}]^+$ . Addition of two equivalents of triphenylphosphine to heated pyridine solutions of silver(I) chloride or bromide, produces crystals of  $[\text{XAg}(\text{py})(\text{PPh}_3)_2]$  ( $X = \text{Cl}^-$  or  $\text{Br}^-$ ) on standing (Engelhardt *et al.*, 1989). The structures are isomorphous, with a mononuclear trigonal planar geometry. However, for  $X = \text{I}^-$ , despite the use of a considerable range of triphenylphosphine stoichiometric ratios, a mixed-base complex, beyond the equimolar complex  $[\text{AgI}(\text{py})(\text{PPh}_3)]$ , was unobtainable.



Complexes  $[\text{XAg}(\text{py})_2(\text{PPh}_3)]$  can be obtained by the crystallization of stoichiometric mixtures of silver(I) halides and triphenylphosphine in pyridine (Engelhardt *et al.*, 1989). Although the resulting complexes are of overall 1:2:1 AgX:py:PPh<sub>3</sub> stoichiometry, they comprise a 1:1:1  $\mu, \mu'$ -dihalo-bridged dimer,  $[\mu\text{-XAg}(\text{py})(\text{PPh}_3)_2]_2$ , solvated with an additional mole of pyridine per Ag atom. Thus, in pyridine solution the existence of monomeric  $[\text{AgX}(\text{py})_2(\text{PPh}_3)]$  was postulated (Gotsis *et al.*, 1989).

While the number of structurally characterized silver(I) halide complexes with mixed phosphorus and nitrogen bases are few, complexes with non-coordinating anions are known. In the centrosymmetric title compound, (I), the Ag atom is coordinated by one phosphine ligand, one pyridine ligand and two iodide anions, forming a distorted tetrahedral coordination (Table 1). The Ag–P distance is 2.4489 (12) Å, the Ag–N distance 2.392 (3) Å and the Ag–I distances are 2.8402 (14) and 2.8644 (8) Å.

The differences in Ag–I bond distances are larger than 3 s.u. of the bond lengths (Table 1). Previously, dimers with

different Ag–X bond lengths were described as partial separation of the dimer into monomers (Bowmaker *et al.*, 1996). Similar distortions are observed here.

A study on the solution behaviour of  $[L_nAgX]$  complexes was initiated by Muetterties & Alegrianti (1972). A series of  $[AgX\{P(4-MeC_6H_4)_3\}_n]$  complexes, where  $n = 2-4$  and  $X$  includes a wide range of counter-anions, was studied by  $^{31}P$  NMR spectroscopy. The ligands were labile in all the complexes studied, so that the first-order P–Ag coupling was not resolved above *ca* 203 K. Rapid ligand-exchange reactions have been reported for all  $^{31}P$  NMR investigations of ionic  $Ag^I$  monodentate phosphine complexes, thus making NMR spectroscopy of limited use for these complexes.

### Experimental

Silver iodide (0.100 g, 0.43 mmol) and tri-*p*-tolylphosphine (0.130 g, 0.43 mmol) were suspended in pyridine (5 ml). The mixture was heated to give a clear colourless solution. Colourless crystals of the title compound suitable for X-ray crystallography were obtained by slow evaporation.

#### Crystal data

$C_{52}H_{52}Ag_2I_2N_2P_2$	$V = 1258.4 (6) \text{ \AA}^3$
$M_r = 1236.44$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 1.632 \text{ Mg m}^{-3}$
$a = 10.006 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 11.957 (2) \text{ \AA}$	$\mu = 2.10 \text{ mm}^{-1}$
$c = 12.184 (2) \text{ \AA}$	$T = 298 (2) \text{ K}$
$\alpha = 104.67 (3)^\circ$	Block, colourless
$\beta = 113.24 (3)^\circ$	$0.44 \times 0.24 \times 0.22 \text{ mm}$
$\gamma = 96.44 (3)^\circ$	

#### Data collection

Bruker SMART CCD area-detector diffractometer	6862 measured reflections
$\varphi$ and $\omega$ scans	4400 independent reflections
Absorption correction: multi-scan (SADABS; Bruker, 2004)	3631 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.440$ , $T_{\max} = 0.629$	$R_{\text{int}} = 0.015$
	$\theta_{\text{max}} = 25^\circ$

#### Refinement

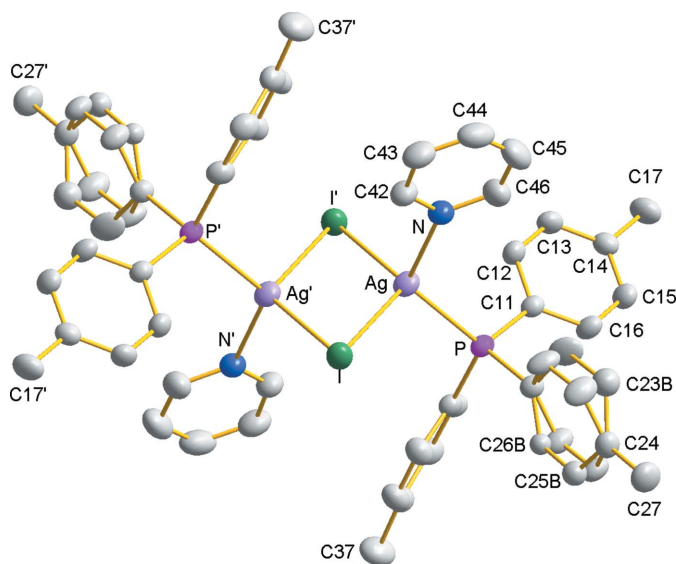
Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0385P)^2 + 0.8633P]$
$R[F^2 > 2\sigma(F^2)] = 0.03$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.078$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 1.05 \text{ e \AA}^{-3}$
4400 reflections	$\Delta\rho_{\text{min}} = -0.51 \text{ e \AA}^{-3}$
295 parameters	
H-atom parameters constrained	

**Table 1**

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

Ag–N	2.392 (3)	Ag–I	2.8644 (8)
Ag–P	2.4489 (12)	Ag $\cdots$ Ag $^i$	3.1138 (8)
Ag–I $^i$	2.8402 (14)		
N–Ag–P	117.09 (9)	P–Ag–I	109.32 (3)
N–Ag–I $^i$	107.99 (8)	I $^i$ –Ag–I	113.84 (4)
P–Ag–I $^i$	111.63 (4)	Ag $^i$ –I–Ag	66.16 (4)
N–Ag–I	96.24 (8)		
N–Ag–I–Ag $^i$	112.83 (9)	I $^i$ –Ag–I–Ag $^i$	0
P–Ag–I–Ag $^i$	–125.58 (4)		

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



**Figure 1**

The molecular structure of (I), showing 30% 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. Primed atoms are generated by the symmetry code  $(1 - x, -y, 1 - z)$ . Both disorder components are shown.

The methyl and aromatic H atoms were placed in geometrically idealized positions ( $C-H = 0.92-0.98 \text{ \AA}$ ) and constrained to ride on their parent atoms, with  $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(\text{methyl C})$  or  $1.2U_{\text{eq}}(\text{aromatic C})$ . Methyl H atoms were placed in idealized positions and the torsion angles were refined to fit the electron density. Disordered benzene ring atoms C22, C23, C25 and C26, with their attached H atoms, were refined over two sites each, with occupancies 0.81 (2) and 0.19 (2). The highest residual electron-density peak is located  $1.04 \text{ \AA}$  from I.

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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