

The X-Ray Structure of μ -Tetraphenyldiphosphine-bis-(tripyridinesilver(I)) Perchlorate, $[(C_5H_5N)_3AgP_2(C_6H_5)_4Ag(C_5H_5N)_3](ClO_4)_2$

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The determination of the crystal structure of $[P_2(C_6H_5)_4Ag_2(C_5H_5N)_6](ClO_4)_2$ was undertaken as a part of a research programme that deals with complex formation between group VB donors and silver(I) in pyridine solution. It is of interest to examine the correlation between thermodynamic parameters such as the enthalpy and entropy of complex formation in solution, and structural properties such as coordination geometry and steric effects.¹ The latter properties can be established in the solid state by diffraction methods.

Experimental

To a 1.0 M solution of $AgClO_4$ in pyridine was added 0.5 mol of $P(C_6H_5)_2H$. The phosphine was oxidized to diphosphine with reduction of silver, and the metallic silver was filtered off. After about one week, small yellow needles were formed and were analyzed by means of single crystal diffractometry. The crystal used for X-ray data collection was cut to an approximate size of $0.42 \times 0.26 \times 0.31$ mm. The final cycle of full matrix refinement included atomic coordinates and anisotropic temperature factors for the non-hydrogen atoms, and calculated positions for the hydrogen atoms with fixed temperature factors.

Results and discussion

A summary of crystallographic data is given in Table 1 and atomic coordinates with equivalent

Table 1. Summary of crystal data, intensity data collection and structure refinement.

(a) <i>Crystal data</i>	
Formula	$C_{54}H_{50}Ag_2Cl_2N_6O_8P_2$
Mol.wt.	1197.8
Crystal system	monoclinic
Space group	$P2_1/c$
$a/\text{Å}$	14.03(2)
$b/\text{Å}$	10.27(1)
$c/\text{Å}$	19.27(2)
$\beta/^\circ$	91.19(9)
Z	2
$d_{\text{calc}}/\text{g cm}^{-3}$	1.51
Radiation	$MoK\alpha$ ($\lambda = 0.71069 \text{ Å}$)
$\mu(MoK\alpha)/\text{cm}^{-1}$	8.4
(b) <i>Data collection and structure refinement</i> ^a	
2θ scan speed/ $^\circ \text{ min}^{-1}$	2.5-29.3 ($\theta/2\theta$)
No. of data collected	6860 ($2\theta \leq 55^\circ$)
No. of observed data	3328 ($I_{\text{obs}} > 3\sigma(I_{\text{obs}})$)
R -int%	2.2
Abs. correction	empirical ^b
Structure solution	SHELXS-86 (Patterson) ^b
$R/\%$	5.3
$R_w/\%$	6.0

^aPrograms used: LELA^{7,8} and those in Ref. 9; scattering factors taken from Ref. 10. ^bMax. reduction in $I_{\text{obs}} = 10\%$.

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Table 2. Fractional coordinates and equivalent isotropic temperature factors¹¹ for C₅₄H₅₀Ag₂Cl₂N₆O₈P₂.

Atom	x	y	z	B/Å ²
Ag	0.22213(3)	-0.00641(5)	1.04021(2)	4.15(1)
P	0.0700(1)	0.0271(1)	0.97663(7)	3.05(4)
Cl	0.4053(2)	0.6149(2)	0.8448(1)	5.88(6)
C 1	0.0570(4)	-0.0500(5)	0.8903(3)	3.3(1)
C 2	-0.0109(5)	-0.0065(6)	0.8415(3)	4.1(2)
C 3	-0.0172(6)	-0.0665(7)	0.7765(3)	4.9(2)
C 4	0.0444(6)	-0.1668(7)	0.7598(3)	5.2(2)
C 5	0.1103(6)	-0.2104(7)	0.8084(4)	5.4(2)
C 6	0.1178(5)	-0.1545(6)	0.8739(3)	4.3(2)
C 7	0.0552(4)	0.2013(5)	0.9546(3)	3.5(2)
C 8	-0.0321(5)	0.2696(6)	0.9514(3)	3.9(2)
C 9	-0.0343(6)	0.3999(7)	0.9300(3)	4.7(2)
C 10	0.0475(7)	0.4625(7)	0.9112(3)	5.2(2)
C 11	0.1348(7)	0.3999(7)	0.9137(4)	5.8(2)
C 12	0.1393(5)	0.2666(6)	0.9369(3)	4.6(2)
N 13	0.2692(4)	-0.2094(5)	1.0838(3)	4.8(2)
C 14	0.2767(5)	-0.2377(8)	1.1519(4)	5.5(2)
C 15	0.3096(6)	-0.3568(10)	1.772(5)	6.8(3)
C 16	0.3390(6)	-0.4495(10)	1.1311(7)	7.5(3)
C 17	0.3334(6)	-0.4245(8)	1.0621(6)	6.6(3)
C 18	0.2988(5)	-0.3025(7)	1.0399(4)	5.5(2)
N 19	0.2382(4)	0.1532(5)	1.1309(3)	4.9(2)
C 20	0.2969(7)	0.1332(8)	1.1849(5)	7.3(3)
C 21	0.2960(9)	0.2146(10)	1.2438(5)	8.9(4)
C 22	0.2304(8)	0.3123(9)	1.2470(5)	7.5(3)
C 23	0.1727(7)	0.3346(8)	1.1922(4)	6.1(2)
C 24	0.1767(5)	0.2509(7)	1.1364(4)	5.2(2)
N 25	0.3572(4)	0.0522(6)	0.9761(3)	5.5(2)
C 26	0.3800(6)	-0.0137(9)	0.9179(5)	6.9(3)
C 27	0.4386(7)	0.0406(10)	0.8676(5)	7.9(3)
C 28	0.4742(6)	0.1646(10)	0.8791(6)	8.5(4)
C 29	0.4523(7)	0.2275(10)	0.9369(7)	8.6(4)
C 30	0.3945(6)	0.1692(9)	0.9857(5)	6.9(3)
O 1	0.4711(7)	0.676(1)	0.8839(9)	22.8(7)
O 2	0.4395(7)	-0.447(1)	0.7905(5)	18.6(5)
O 3	0.3934(16)	-0.024(2)	0.3877(9)	29.0(5)
O 4	0.3172(7)	-0.337(1)	0.8451(6)	19.5(6)

Fig. 1. Stereoscopic view of the [P₂(C₆H₅)₄Ag₂(C₅H₅N)₆]²⁺ ion. The atoms are depicted as spheres of radius 0.08 Å for silver(I), 0.11 Å for phosphorus and 0.14 Å for carbon and nitrogen. The thin lines represent the coordination bonds to the silver atoms.

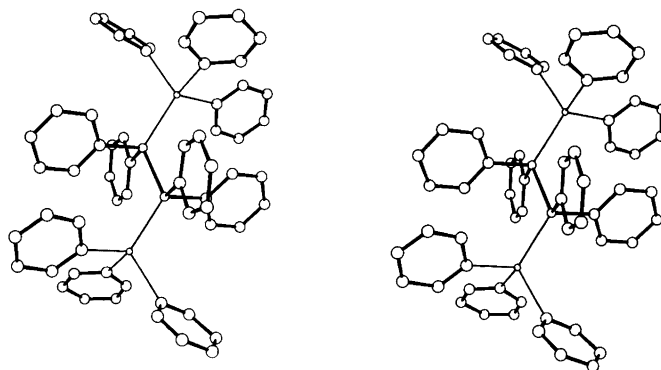


Table 3. Selected distances (Å) and angles (°) in $C_{54}H_{50}Ag_2Cl_2N_6O_6P_2$.

Ag-P	2.463(2)	P ⁽ⁱ⁾ -P-Ag	121.4(1)
P-P ⁽ⁱ⁾	2.249(3)	P ⁽ⁱ⁾ -P-C1	100.6(2)
Ag-N13	2.338(6)	P ⁽ⁱ⁾ -P-C7	103.7(2)
Ag-N19	2.362(6)	Ag-P-C1	117.2(2)
Ag-N25	2.403(5)	Ag-P-C7	110.0(2)
P-C1	1.849(5)	C1-P-C7	101.5(2)
P-C7	1.849(6)	P-Ag-N13	122.6(1)
Cl-O1	1.336(13)	P-Ag-N19	109.5(1)
Cl-O2	1.325(11)	P-Ag-N25	113.6(1)
Cl-O3	1.262(18)	N13-Ag-N19	109.0(2)
Cl-O4	1.331(10)	N13-Ag-N25	101.3(3)
		N19-Ag-N25	98.2(2)

Symmetry code: ⁽ⁱ⁾ $\bar{x}, \bar{y}, 2-z$

temperature factors for the non-hydrogen atoms are listed in Table 2. Selected distances and angles are given in Table 3. A list of structure factors, hydrogen coordinates and anisotropic temperature factors is available from the authors on request.

The compound investigated consists of discrete $[P_2(C_6H_5)_4Ag_2(C_3H_5N)_6]^{2+}$ and ClO_4^- ions. The cation (Fig. 1) consists of two silver(I) ions, each coordinated tetrahedrally to three pyridine molecules (via N) and one phosphorus atom. Each phosphorus atom is surrounded by a tetrahedron comprising one silver ion, the other phosphorus atom and two tertiary carbon atoms of the phenyl rings. The configurations about the Ag-P and the P-P bonds are both close to the ethane-like staggered configuration. According to the space group symmetry the cation is centrosymmetric about the P-P bond, and the P-P distance of 2.249(2) Å is well within the earlier-reported range of values of 2.12–2.35 Å.^{2,3}

The Ag-P distances in previously reported structures vary widely, depending on the number of phosphorus atoms coordinated to silver(I).⁴ Table 4 gives Ag-P distances for a number of different silver(I) phosphine compounds in which the silver ions are tetrahedrally coordinated to one or two phosphorus atoms. The Ag-P distance found in this work is among the longest reported for structures with one phosphorus coordinated to silver. The mean Ag-N distance, 2.372(3) Å, is also significantly greater than that found in tetrapyridinesilver(I) perchlorate, viz. 2.322(3) Å.⁵ This is most probably due to differ-

Table 4. Distances (Å) in some silver(I) phosphine complexes; *n* denotes the number of phosphorus atoms coordinated to silver. Pairs of distances are maximum and minimum values.

Compound	Ag-P	<i>n</i>	Ref.
AgNO ₃ PPh ₃	2.369(3)	1	12
AgSCNP(<i>n</i> -Pr) ₃	2.48(3)	1	13
AgClPEt ₃	2.390(2)	1	14
AgBrPEt ₃	2.402(5)	1	14
AgIPEt ₃	2.438(2)	1	15
AgClPPh ₃	2.376(3)	1	16
	2.388(3)		
AgBrPPh ₃	2.415(5)	1	17
	2.429(2)		
AgIPPh ₃ (cubane)	2.456(5)	1	18
	2.462(5)		
[Ag ₂ (P ₂ Ph ₄)Py ₆](ClO ₄) ₂	2.463(2)	1	this work
(AgPPh ₃) ₄ (C ₁₂ H ₆ O ₄) ₂ (C ₆ H ₆) ₂	2.342(4)	1	19
	2.378(5)		
AgSCN(PPh ₃) ₂	2.455(3)	2	20
	2.503(5)		
AgCl(PPh ₃) ₂	2.467(2)	2	21
	2.472(2)		
AgBr(PPh ₃) ₂ .CHCl ₃	2.513(7)	2	17
	2.479(6)		
AgClPSP ^a	2.481(4)	2	22
	2.461(4)		
AgIPSP ^a	2.461(2)	2	23
	2.461(2)		
AgClPC ₅ P ^b	2.472(3)	2	24
	2.499(4)		

^aPSP = bis(diphenylphosphinoethyl)sulfide. ^bPC₅P = 1,5-bis(diphenylphosphino)pentane.

ent donor effects of the three pyridine molecules and the phosphorus atom.

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