

## Crystal and Molecular Structures of Two Complexes of Diphenyl(2-pyridyl)phosphine (L): [AuClL] and [Ag<sub>2</sub>Cl<sub>2</sub>L<sub>3</sub>]

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The reaction of the ligand diphenyl(2-pyridyl)phosphine (L) with H<sub>2</sub>AuCl<sub>4</sub> and AgCl affords the complexes [AuClL] and [Ag<sub>2</sub>Cl<sub>2</sub>L<sub>3</sub>] respectively. The crystal structures of these two complexes have been determined from four-circle diffractometer data; [AuClL] is orthorhombic, space group *Pnma*, with  $a = 11.774(3)$ ,  $b = 12.617(3)$ , and  $11.114(6)$  Å,  $Z = 4$ , and  $R = 0.052$  for 1 358 observed reflections; [Ag<sub>2</sub>Cl<sub>2</sub>L<sub>3</sub>] is monoclinic, space group *P2<sub>1</sub>/c* with  $a = 14.599(3)$ ,  $b = 18.388(5)$ , and  $c = 21.134(4)$  Å,  $\beta = 125.12(1)^\circ$ ,  $Z = 4$ , and  $R = 0.060$  for 5 180 observed reflections. In the gold complex the phosphorus of L alone is bonded to the gold atom which assumes a linear geometry with Au-Cl 2.286(4) Å and Au-P 2.234(4) Å. The silver complex contains molecules in which two silver atoms are held together by two chloride bridges. One of the silver atoms is bonded to two L molecules through the phosphorus atom, while the other silver atom is bonded to a L molecule as well as loosely bonded to the nitrogen atom of one of the ligands co-ordinated to the first silver atom. The silver atoms assume a tetrahedral co-ordination with Ag-Cl 2.701(4), 2.618(8), 2.638(4), and 2.601(9) Å; Ag-P 2.432(3), 2.436(4), and 2.452(3) Å; and Ag-N 2.451(9) Å.

WITH both a nitrogen-donor atom and a phosphorus-donor atom present in the molecule, diphenyl(2-pyridyl)phosphine (L) is potentially a bidentate chelating ligand. In a preliminary report<sup>1</sup> the complexes were divided on the basis of their i.r. spectra into those in which the co-ordination is essentially through the nitrogen atom and those linked through the phosphorus atom. The gold(I) chloride and the silver(I) chloride complexes were assigned to the second group. The crystal structures of [AuClL] and [Ag<sub>2</sub>Cl<sub>2</sub>L<sub>3</sub>] are reported here.

### EXPERIMENTAL

**Reactions of Diphenyl(2-pyridyl)phosphine.**—With chloroauric acid. The compound diphenyl(2-pyridyl)phosphine (0.57 g, 2.2 mmol) in ethanol (5 cm<sup>3</sup>) was added dropwise with stirring to a solution of chloroauric acid (0.41 g, 1.0 mmol) in ethanol (5 cm<sup>3</sup>). The brown colour of the chloroauric acid began to fade as colourless crystals separated from the solution. The product was recrystallised from benzene and dried *in vacuo* over P<sub>2</sub>O<sub>5</sub> at ca. 90 °C. Yield: 0.38 g.

**With silver chloride.** Silver chloride was freshly prepared by reaction of an aqueous solution of silver nitrate with dilute hydrochloric acid, in the dark. The precipitate was washed with distilled water, dried in an oven, and 0.17 g (1.2 mmol) was added to a solution of diphenyl(2-pyridyl)phosphine (0.64 g, 2.4 mmol) in ethanol (25 cm<sup>3</sup>). The suspension was refluxed in the dark for 8 h, after which the unreacted silver chloride was filtered off. On cooling the filtrate, a colourless polycrystalline mass was deposited. This was recrystallised from a chloroform-benzene-diethyl ether (1 : 1 : 1) mixture and dried over P<sub>2</sub>O<sub>5</sub> *in vacuo* at ca. 80 °C. Yield: 0.66 g. The recrystallised product was a white powder but under a microscope a few well formed crystals were found. One of these was used for the structural determination.

**Crystallographic Study.**—Crystal data for [AuClL] (1) and [Ag<sub>2</sub>Cl<sub>2</sub>L<sub>3</sub>] (2) are given in Table 1, with details of intensity measurements. Data were collected with a Syntex P2<sub>1</sub> diffractometer, which was used also for determination of unit-cell parameters by a least-squares fit to the reflecting positions of 15 strong reflections in each case. A

Patterson synthesis was used to locate the heavy atoms, while Fourier maps were used to locate all the other non-hydrogen atoms. No crystal decomposition was detected.

The gold complex has crystallographic *m* symmetry. Electron densities for the atoms in the pyridyl ring were

TABLE 1  
Crystal data for [AuClL] and [Ag<sub>2</sub>Cl<sub>2</sub>L<sub>3</sub>]

	(1) *	(2) *
Formula	C <sub>17</sub> H <sub>14</sub> AuClNP	C <sub>51</sub> H <sub>42</sub> Ag <sub>2</sub> Cl <sub>2</sub> N <sub>3</sub> P <sub>3</sub>
<i>M</i>	495.6	1 075.9
System	Orthorhombic	Monoclinic
Absences	0 <i>kl</i> , $k + l = 2n + 1$ $h\bar{k}0$ , $h = 2n + 1$	$h0l$ , $l = 2n + 1$ $0k0$ , $k = 2n + 1$
Space group	<i>Pnma</i>	<i>P2<sub>1</sub>/c</i>
<i>a</i> /Å	11.774(3)	14.599(3)
<i>b</i> /Å	12.617(3)	18.388(5)
<i>c</i> /Å	11.114(6)	21.134(4)
$\beta/^\circ$	90	125.12(1)
<i>U</i> /Å <sup>3</sup>	1 650.9(5)	4 662(1)
$\mu$ (Mo- <i>K</i> $\alpha$ )	91.32	7.34
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.99	1.53
<i>D<sub>m</sub></i> /g cm <sup>-3</sup>	1.96	
<i>R</i> (final)	0.052	0.060
Scan range (max. 2 $\theta$ )	55	50
Reflections:		
all	2 194	7 835
with $I > 3\sigma(I)$	1 358	5 180

\* For both (1) and (2):  $Z = 4$ ; radiation, Mo-*K* $\alpha$  with graphite monochromator,  $\lambda = 0.710 69$  Å.

mostly about half the values for those in the two phenyl rings, and they were treated as disordered, with 50% occupancy. Three variations for the pyridyl ring were examined: (i) with all the atoms off the symmetry plane, (ii) with only the carbon atom bonded to the phosphorus atom in the symmetry plane, and (iii) with this carbon and that in a *para* position to it in the symmetry plane. All gave identical final conventional *R* values of 0.052. The last option is reported here. Refinement was also attempted in the non-centrosymmetric space group *Pn2<sub>1</sub>a* with an ordered pyridyl ring, but this failed to converge satisfactorily. The space group *Pnma* was therefore finally selected. Hydrogen atoms were not included.

For the silver complex, refinement was straightforward except that the nitrogen atom could not be identified in

any of the six possible positions associated with P(2). It is presumably randomly distributed. Hydrogen atoms were inserted in calculated positions, and were then successfully refined.

Anisotropic thermal parameters were used for all non-hydrogen atoms except for the four atoms of the pyridyl ring not on the symmetry plane in the gold(I) chloride complex. Scattering factors from ref. 2 were used, in the analytical form. An absorption correction was carried out with the program ABSCOR.<sup>3</sup> The 'X-RAY '76' programs<sup>4</sup> were mainly used, on a Burroughs B6700 computer, with final refinement for (2) by 'X-RAY '72' on a CDC 7600 computer.

Table 2 contains atomic co-ordinates and Table 3 bond

TABLE 2

Fractional atomic co-ordinates ( $\times 10^4$ ) with standard deviations in parentheses

Atom	x	y	z
(a) For [AuClL]			
Au	4 675.6(5)	2 500.0	4 057.0(5)
Cl	5 527(3)	2 500	5 771(3)
P	3 789(3)	2 500	2 414(4)
C(11)	2 932(9)	1 193(12)	2 280(10)
C(12)	2 294(11)	1 052(13)	1 362(10)
C(13)	1 604(12)	84(15)	1 312(14)
C(14)	1 573(20)	-734(21)	2 138(21)
C(15)	2 289(32)	-663(35)	2 999(29)
C(16)	2 966(26)	320(29)	3 073(22)
C(21)	4 630(15)	2 500	1 146(12)
C(22) <sup>a,b</sup>	5 334(36)	1 565(42)	1 089(38)
C(23) <sup>a</sup>	5 985(43)	1 476(49)	102(45)
C(24)	5 922(28)	2 500	-701(26)
C(25) <sup>a</sup>	5 069(45)	3 121(47)	-731(47)
C(26) <sup>a,b</sup>	4 491(37)	3 260(43)	305(42)
(b) For [Ag <sub>2</sub> Cl <sub>2</sub> L <sub>3</sub> ]			
Ag(1)	1 933.6(6)	2 423.7(4)	196.8(4)
Ag(2)	-115.5(7)	2 886.6(5)	165.8(5)
Cl(1)	-113(3)	1 948(2)	-778(2)
Cl(2)	1 851(2)	2 634(2)	1 428(1)
P(1)	3 268(2)	1 488(1)	424(1)
P(2)	-1 498(2)	2 579(1)	420(1)
P(3)	1 948(2)	3 685(1)	-175(1)
N(1)	-65(6)	3 994(4)	-459(4)
N(2)	3 482(7)	0(4)	714(5)
C(111)	3 047(8)	631(5)	758(5)
C(112)	3 267(9)	-621(5)	963(6)
C(113)	2 619(9)	-623(6)	1 232(7)
C(114)	2 210(10)	21(7)	1 293(7)
C(115)	2 389(9)	664(6)	1 039(7)
C(121)	4 750(8)	1 691(5)	1 125(5)
C(122)	5 503(9)	1 222(6)	1 681(6)
C(123)	6 605(10)	1 413(8)	2 200(7)
C(124)	6 973(10)	2 094(9)	2 171(8)
C(125)	6 228(12)	2 564(8)	1 615(9)
C(126)	5 118(10)	2 379(6)	1 092(7)
C(131)	3 210(8)	1 275(5)	-440(5)
C(132)	3 926(9)	807(6)	-440(6)
C(133)	3 861(11)	664(7)	-1 094(8)
C(134)	3 103(10)	1 011(6)	-1 769(6)
C(135)	2 381(9)	1 499(6)	-1 784(5)
C(136)	2 423(8)	1 625(5)	-1 130(5)
C(211)	-1 285(8)	1 665(5)	826(5)
C(212)	-727(9)	1 171(6)	680(7)
C(213)	-642(11)	446(8)	931(9)
C(214)	-1 068(13)	262(7)	1 311(10)
C(215)	-1 609(13)	759(8)	1 454(10)
C(216)	-1 729(11)	1 456(6)	1 194(7)
C(221)	-2 962(7)	2 544(5)	-416(5)
C(222)	-3 823(8)	2 445(6)	-323(6)
C(223)	-4 909(8)	2 399(6)	-978(7)
C(224)	-5 139(8)	2 457(6)	-1 694(6)
C(225)	-4 293(9)	2 562(6)	-1 792(5)
C(226)	-3 195(8)	2 605(5)	-1 137(5)

TABLE 2 (continued)

Atom	x	y	z
C(231)	-1 543(9)	3 151(5)	1 115(5)
C(232)	-2 307(9)	3 662(5)	858(6)
C(233)	-2 314(12)	4 120(7)	1 376(9)
C(234)	-1 517(14)	4 036(8)	2 152(9)
C(235)	-716(12)	3 524(9)	2 408(7)
C(236)	-724(10)	3 074(7)	1 890(6)
C(311)	2 308(8)	3 779(5)	-864(5)
C(312)	1 538(10)	3 594(6)	-1 627(6)
C(313)	1 775(14)	3 596(8)	-2 162(7)
C(314)	2 844(16)	3 799(8)	-1 921(9)
C(315)	3 608(12)	3 977(7)	-1 182(10)
C(316)	3 364(9)	3 963(6)	-642(6)
C(321)	648(7)	4 223(5)	-630(5)
C(322)	430(8)	4 818(5)	-1 082(6)
C(323)	-547(9)	5 209(5)	-1 373(6)
C(324)	-1 271(8)	4 981(6)	-1 212(6)
C(325)	-1 016(8)	4 384(6)	-753(6)
C(331)	2 988(7)	4 245(5)	648(5)
C(332)	3 122(8)	4 985(5)	577(6)
C(333)	3 945(9)	5 368(5)	1 218(7)
C(334)	4 632(10)	5 028(8)	1 919(7)
C(335)	4 498(11)	4 304(7)	1 986(7)
C(336)	3 684(8)	3 913(5)	1 351(6)
H(112)	3 595(70)	-1 047(44)	899(47)
H(113)	2 522(78)	-1 063(50)	1 503(53)
H(114)	1 859(65)	63(42)	1 530(44)
H(115)	2 269(115)	1 071(72)	1 194(77)
H(122)	5 332(67)	838(44)	1 730(46)
H(123)	7 124(87)	1 216(55)	2 695(59)
H(124)	7 712(79)	2 257(51)	2 555(53)
H(125)	6 314(85)	2 938(56)	1 551(57)
H(126)	4 713(66)	2 547(43)	693(44)
H(132)	4 428(66)	665(42)	-25(46)
H(133)	4 245(88)	420(57)	-1 162(60)
H(134)	3 044(68)	892(43)	-2 217(46)
H(135)	1 876(68)	1 744(43)	-2 234(46)
H(136)	1 921(85)	1 910(55)	-1 062(58)
H(212)	-401(75)	1 263(48)	457(51)
H(213)	-303(92)	138(59)	740(63)
H(214)	-1 013(95)	-156(61)	1 465(64)
H(215)	-1 916(67)	638(43)	1 771(46)
H(216)	-2 157(104)	1 810(68)	1 280(70)
H(222)	-3 633(66)	2 372(43)	207(45)
H(223)	-5 489(71)	2 389(47)	-931(48)
H(224)	-5 797(79)	2 390(52)	-2 141(54)
H(225)	-4 418(75)	2 566(51)	-2 277(52)
H(226)	-2 676(72)	2 643(48)	-1 212(49)
H(232)	-2 756(76)	3 715(49)	531(51)
H(233)	-2 886(75)	4 387(48)	1 204(51)
H(234)	-1 543(97)	4 354(62)	2 464(66)
H(235)	-253(88)	3 578(57)	2 934(60)
H(236)	-175(82)	2 674(52)	2 094(55)
H(312)	913(76)	3 437(50)	-1 747(52)
H(313)	1 182(89)	3 518(57)	-2 763(61)
H(314)	2 887(91)	3 778(56)	-2 378(61)
H(315)	4 217(89)	4 090(56)	-959(60)
H(316)	3 768(69)	4 173(45)	-238(48)
H(322)	900(63)	4 919(41)	-1 211(43)
H(323)	-624(70)	5 569(45)	-1 682(48)
H(324)	-1 851(88)	5 177(56)	-1 379(60)
H(325)	-1 438(77)	4 194(50)	-584(53)
H(332)	2 637(74)	5 175(47)	87(51)
H(333)	3 991(64)	5 850(41)	1 158(43)
H(334)	5 231(65)	5 334(42)	2 418(45)
H(335)	5 002(82)	4 058(51)	2 482(55)
H(336)	3 601(73)	3 390(47)	1 410(49)

<sup>a</sup> Occupancy 0.5. <sup>b</sup> One of these is a nitrogen atom (see text).

lengths and angles of the gold(I) chloride complex, while the corresponding values for the silver(I) chloride complex are given in Table 4. Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 23194 (52 pp).\*

\* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

TABLE 3

Bond lengths (Å) and angles (°) for [AuClL] (1) with standard deviations in parentheses

Au-Cl	2.286(4)	C(15)-C(16)	1.390(51)
Au-P	2.234(4)	C(16)-C(11)	1.347(31)
P-C(11)	1.818(13)	C(21)-C(22) *	1.37(5)
P-C(21)	1.832(17)	C(22) *-C(23)	1.43(7)
C(11)-C(12)	1.355(17)	C(23)-C(24)	1.48(6)
C(12)-C(13)	1.393(21)	C(24)-C(25)	1.28(6)
C(13)-C(14)	1.332(29)	C(25)-C(26) *	1.43(7)
C(14)-C(15)	1.360(45)	C(26) *-C(21)	1.31(5)
Cl-Au-P	178.0(2)	C(15)-C(16)-C(11)	120.2(26)
Au-P-C(11)	111.9(4)	C(16)-C(11)-C(12)	119.6(17)
Au-P-C(21)	114.6(6)	C(21)-C(22)-C(23)	117.8(39)
C(11)-P-C(21)	105.9(4)	C(22)-C(23)-C(24)	115.3(43)
C(11)-P-C(11)	106.1(6)	C(23)-C(24)-C(25)	118.5(39)
C(11)-C(12)-C(13)	119.3(13)	C(24)-C(25)-C(26)	117.6(46)
C(12)-C(13)-C(14)	121.3(17)	C(25)-C(26)-C(21)	120.4(42)
C(13)-C(14)-C(15)	119.0(25)	C(26)-C(21)-C(22)	122.5(30)
C(14)-C(15)-C(16)	120.1(30)		

\* One of these is a nitrogen atom. See text.

TABLE 4

Principal bond lengths (Å) and angles (°) for [Ag<sub>2</sub>Cl<sub>2</sub>L<sub>3</sub>] (2) with standard deviations in parentheses

Bond lengths			
Ag(1)-Ag(2)	3.074(2)	P(1)-C(111)	1.83(1)
Ag(1)-Cl(1)	2.618(8)	P(1)-C(121)	1.82(1)
Ag(1)-Cl(2)	2.701(4)	P(1)-C(131)	1.82(1)
Ag(1)-P(1)	2.432(3)	P(2)-C(211)	1.83(1)
Ag(1)-P(3)	2.452(3)	P(2)-C(221)	1.83(1)
Ag(2)-Cl(1)	2.638(4)	P(2)-C(231)	1.84(1)
Ag(2)-Cl(2)	2.601(9)	P(3)-C(311)	1.82(1)
Ag(2)-P(2)	2.436(4)	P(3)-C(321)	1.85(1)
Ag(2)-N(1)	2.451(9)	P(3)-C(331)	1.83(1)
Bond angles			
Ag(2)-Ag(1)-Cl(1)	54.5(1)	Ag(1)-Cl(2)-Ag(2)	70.86(7)
Ag(2)-Ag(1)-Cl(2)	53.05(6)	Ag(1)-Cl(2)-C(111)	112.7(4)
Ag(2)-Ag(1)-P(1)	149.27(8)	Ag(1)-P(1)-C(121)	117.2(3)
Ag(2)-Ag(1)-P(3)	85.33(8)	Ag(1)-P(1)-C(131)	112.6(3)
Cl(1)-Ag(1)-Cl(2)	98.1(1)	C(111)-P(1)-C(121)	104.6(4)
Cl(1)-Ag(1)-P(1)	110.0(1)	C(111)-P(1)-C(131)	106.5(5)
Cl(1)-Ag(1)-P(3)	106.25(9)	C(121)-P(1)-C(131)	102.1(5)
Cl(2)-Ag(1)-P(1)	112.70(9)	Ag(2)-P(2)-C(211)	122.2(5)
Cl(2)-Ag(1)-P(3)	100.7(1)	Ag(2)-P(2)-C(221)	116.8(4)
P(1)-Ag(1)-P(3)	125.4(1)	Ag(2)-P(2)-C(231)	117.3(4)
Ag(1)-Ag(2)-Cl(1)	53.90(8)	C(211)-P(2)-C(221)	102.1(4)
Ag(1)-Ag(2)-Cl(2)	56.09(8)	C(211)-P(2)-C(231)	103.0(5)
Ag(1)-Ag(2)-P(2)	148.29(7)	C(221)-P(2)-C(231)	103.5(5)
Ag(1)-Ag(2)-N(1)	84.9(2)	Ag(1)-P(3)-C(311)	113.9(3)
Cl(1)-Ag(2)-Cl(2)	100.23(1)	Ag(1)-P(3)-C(231)	118.6(3)
Cl(1)-Ag(2)-P(2)	112.1(1)	Ag(1)-P(3)-C(331)	112.6(3)
Cl(1)-Ag(2)-N(1)	97.1(2)	C(311)-P(3)-C(321)	102.5(5)
Cl(2)-Ag(2)-P(2)	107.4(1)	C(311)-P(3)-C(331)	104.0(5)
Cl(2)-Ag(2)-N(1)	110.1(2)	C(321)-P(3)-C(331)	103.6(4)
P(2)-Ag(2)-N(1)	126.7(2)	C(321)-N(1)-Ag(2)	132.1(6)
Ag(1)-Cl(1)-Ag(2)	71.59(8)	C(325)-N(1)-Ag(2)	110.3(8)

## DISCUSSION

Co-ordination of the N atom of diphenyl(2-pyridyl)-phosphine (L) to a metal ion is expected to shift the i.r. bands of the pyridine ring by 15–30 cm<sup>-1</sup> to higher frequencies.<sup>5,6</sup> Since the pyridine bands at 1565, 1558, 998, and 620 cm<sup>-1</sup> are unaffected by co-ordination of L to AuCl and AgCl, it was concluded that bonding occurs primarily through the P atom.<sup>7</sup>

The reduction of gold(III) compounds to gold(I) by tertiary phosphines is well known, giving compounds of the type [AuX(PR<sub>3</sub>)<sub>2</sub>] (X = halide).<sup>8</sup> Replacement of

one of the phenyl groups of PPh<sub>3</sub> by a pyridyl group does not alter the reducing properties of the phosphine, as shown by the ready formation of [AuClL] from chlorauric acid and L. The structure of [AuClL] is shown in Figure 1. The gold atom is two-co-ordinate

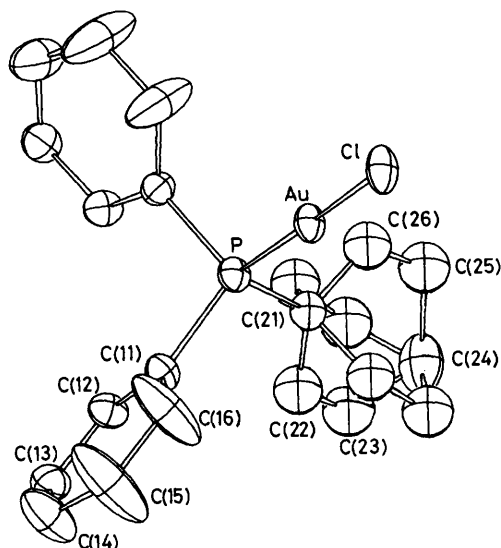


FIGURE 1 View of [AuClL] (1) showing the atomic numbering scheme. All the possible atomic positions of the disordered ring are shown

with a virtually linear geometry (P-Au-Cl 178.0°) as usually observed for Au<sup>I</sup>. The Au-Cl and Au-P bond lengths of 2.286(4) and 2.234(4) Å respectively are very similar to the corresponding values of 2.279(3) and 2.235(3) Å observed in [AuCl(PPh<sub>3</sub>)].<sup>9</sup> These bond distances increase to 2.347(4) Å for Au-Cl in a *trans* position to Au-P, and 2.335(4) Å for Au-P in [AuCl<sub>3</sub>(PPh<sub>3</sub>)].<sup>10</sup>

Bond angles and bond lengths in the two phenyl rings of the ligand are normal. Larger standard deviations are observed for these values in the pyridyl ring because of its disordered nature, which also makes it impractical to identify the nitrogen unequivocally in the ring. Of the two possible positions, one is at 3.73(4) and the other is at 4.50(5) Å from the gold atom. Even the shorter distance is outside the sum of van der Waals radii of 3.7 Å (1.5 Å for nitrogen and 2.2 Å estimated for gold by Duckworth and Stephenson<sup>11</sup>). There is therefore hardly any interaction between the gold and the nitrogen atom. There are also no stray interactions between molecules within the unit cell, which is no doubt the reason for the disorder (Figure 2).

Reaction of the tertiary phosphines with copper(II) and silver(I) halides are known to produce complexes of Cu<sup>I</sup> and Ag<sup>I</sup> of the type M<sub>m</sub>X<sub>m</sub>(PR<sub>3</sub>)<sub>l</sub> where *l*:*m* = 4:1, 3:1, 4:2, 3:2, and 4:4.<sup>12</sup> The structure of di-*μ*-chloro-tris(triphenylphosphine)dycopper(I), [Cu<sub>2</sub>Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>], has been determined<sup>13</sup> but that of the silver complex has not. The former has two of the three phosphine ligands bonded to one of the copper atoms

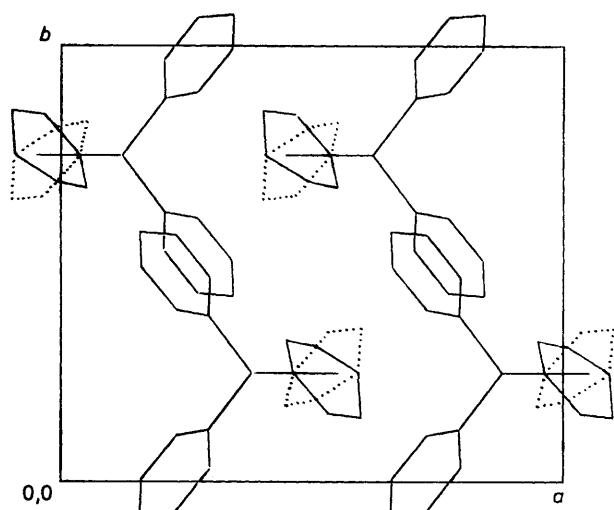


FIGURE 2 Packing diagram for (1), viewed down  $c$ . Both positions of the disordered ring are shown

and the third to the other, so that one metal atom is four- and the other three-co-ordinate.

The molecular structure of  $[Ag_2Cl_2L_3]$  is shown in Figure 3. Like the (triphenylphosphine)copper chloride

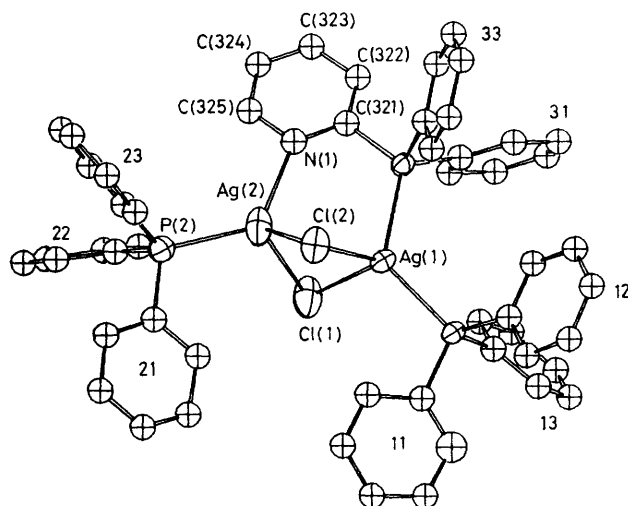


FIGURE 3 View of  $[Ag_2Cl_2L_3]$  (2), showing numbering for the principal atoms and for each ring ( $mn$ ) for C( $mn1-6$ )

complex mentioned above there are two silver atoms held together by two chlorine bridges in each molecule. In addition one of the silver atoms has two of the three ligands L bonded to it and the other silver atom is bonded to the third ligand. All the ligands L are bonded through the phosphorus atom, as previously deduced from the i.r. spectrum. However, one of the two ligands L bonded to the first Ag atom is oriented in such a way that the N atom of the pyridine ring is only 2.451(9) Å from the second Ag atom. Although this distance is much longer than the estimated 2.04 Å for the single Ag-N bond (0.70 for the single covalent radius of nitrogen and 1.34 Å for the metallic single bond of silver<sup>14</sup>), it is much shorter than the sum of van der

Waals radii. This means that one of the silver atoms is straightforwardly four-co-ordinate with two chlorine and two phosphorus atoms while the other silver atom is irregularly four-co-ordinate with one nitrogen, one phosphorus, and two chlorine atoms. This is the first known example of L behaving as a bidentate ligand.

The Ag-Cl bond distances are 2.601(9), 2.618(8), 2.638(4), and 2.701(4) Å with an average value of 2.639 Å. This average value is very similar to the average values of 2.653 and 2.648 Å respectively for the cubane-like  $[{AgCl(PPh_3)}_4]$ <sup>15</sup> and  $[{AgCl(PEt_3)}_4]$ <sup>16</sup> in which all the Cl atoms are bridging. The three Ag-P bond distances of 2.432(3), 2.436(4), and 2.452(3) Å give an average value of 2.440 Å. This value is very close to the estimated one of 2.44 Å for the single Ag-P bond (1.34 Å for Ag and 1.10 Å for P).<sup>14</sup> It is slightly longer than the average values of 2.382 and 2.390 Å for  $[{AgCl(PPh_3)}_4]$  and  $[{AgCl(PEt_3)}_4]$  respectively and is closer to the average Ag-P bond distances of 2.458 and 2.438 Å respectively for the cubane-like  $[{AgI(PPh_3)}_4]$ <sup>17</sup> and  $[{AgI(PEt_3)}_4]$ .<sup>16</sup>

Bond angles around the first Ag atom are between 98.1(1) and 125.4(1)°; the largest value corresponds to the P-Ag-P angle. Those around the second silver atom are between 97.1(2) and 126.7(2)° with the P-Ag-N angle having the highest value. These correspond quite closely to the 87.2–138.9 and 88.2–134.9° ranges observed in  $[{AgCl(PPh_3)}_4]$  and  $[{AgCl(PEt_3)}_4]$  respectively. The overall configurations around the two silver atoms in  $[Ag_2Cl_2L_3]$  are therefore distorted tetrahedra.

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