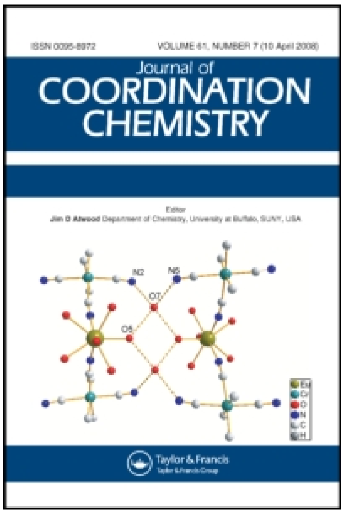

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

X-RAY STRUCTURES OF BIS[(2-AMINOPHENYL)DIPHENYLPHOSPHINE]BIS-(ETHANOL)SILVER(I) NITRATE AND TRIS[(2-AMINOPHENYL)DIPHENYLPHOSPHINE] SILVER(I) NITRATE MONOHYDRATE

Edward R. T. Tiekink[a]
[a] Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia, Australia

To cite this Article Tiekink, Edward R. T.(1993) 'X-RAY STRUCTURES OF BIS[(2-AMINOPHENYL)DIPHENYLPHOSPHINE]BIS-(ETHANOL)SILVER(I) NITRATE AND TRIS[(2-AMINOPHENYL)DIPHENYLPHOSPHINE] SILVER(I) NITRATE MONOHYDRATE', Journal of Coordination Chemistry, 28: 3, 223 — 230

To link to this Article: DOI: 10.1080/00958979308037101

URL: http://dx.doi.org/10.1080/00958979308037101

J. Coord. Chem. 1993, Vol. 28, pp. 223–230
Reprints available directly from the publisher
Photocopying permitted by license only

X-RAY STRUCTURES OF BIS[(2-AMINOPHENYL)DIPHENYLPHOSPHINE]BIS-(ETHANOL)SILVER(I) NITRATE AND TRIS[(2-AMINOPHENYL)DIPHENYLPHOSPHINE] SILVER(I) NITRATE MONOHYDRATE

EDWARD R. T. TIEKINK

Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia 5001, Australia

(Received August 17, 1992; in final form September 17, 1992)

The crystal structures of two Ag(I) salts, $[Ag(LH)_2(EtOH)_2](NO_3)$ (**1**) and $[Ag(LH)_3](NO_3).H_2O$ (**2**) where LH is (2-aminophenyl)diphenylphosphine, have been determined at room temperature. In **1** the Ag atom is coordinated by two P atoms derived from the phosphine ligands (Ag-P(1) 2.433(3) and Ag-P(2) 2.439(3) Å and P(1)-Ag-P(2) 160.1(1)°) and two O atoms derived from two weakly coordinating ethanol molecules (Ag-O(1a) 2.49(1) and Ag-O(2a) 2.75(1) Å). In **2** the three phosphine ligands coordinate *via* the P atoms (Ag-P 2.455(2), 2.462(2) and 2.484(2) Å) which define a trigonal planar geometry about the Ag atom. In neither case was any evidence found for a bonding interaction between the amino-N atom and the Ag atom. Crystals of **1** are monoclinic, space group $P2_1/n$ with unit cell dimensions: $a = 10.272(4)$, $b = 16.358(2)$, $c = 23.709(3)$ Å, $\beta = 101.01(2)°$ and $Z = 4$ and crystals of **2** are triclinic, space group $P\bar{1}$ *with* $a = 11.857(2)$, $b = 21.285(2)$, $c = 11.190(4)$ Å, $\alpha = 91.77(1)$, $\beta = 104.50(2)$, $\gamma = 97.93(1)°$ and $Z = 2$. The structures were each refined by a full-matrix least-squares procedure to final $R = 0.058$ using 2433 reflections for **1** and to $R = 0.069$ using 4428 reflections for **2**.

KEY WORDS: Silver, phosphines, X-ray structures.

INTRODUCTION

Among the many and varied applications of transition metal phosphine complexes is the use of certain derivatives in medicine. Perhaps the most important example is that of the triethylphosphinegold(I) complex, (1-thio-β-D-glucopyranose-2,3,4,6-tetraacetato-*S*)(triethylphosphine)gold(I) (Auranofin), which is in clinical use as an anti-arthritic drug.[1] Gold(I) phosphine complexes have also shown promising activity against tumourous cells and the tetrahedral bis chelated gold(I) complex, $[Au(dppe)_2]^+$ (dppe is 1,2-bis(diphenylphosphine)ethane), was particularly active.[2,3] Subsequently the $[Cu(dppe)_2]^+$[4] and $[Ag(dppe)_2]^+$[5] analogues were shown to possess some activity, but less than that of the Au(I) species. An interesting feature of the $[Ag(dppe)_2]^+$[6] and $[Au(dppe)_2]^+$[7-9] complexes is the presence of tetrahedral metal centres as shown by crystallographic methods. In this context, it was thought of interest to explore the complexation of the Ag(I) cation by the potentially bidentate ligand, (2-aminophenyl)diphenylphosphine (LH), and the results of this study are reported herein. The neutral ligand, LH, has been shown previously to coordinate metal centres exclusively in the bidentate mode *via* the P- and N-donor atoms, i.e., in *cis*-and *trans*-$[Pt(LH)_2]$,[2+10] *cis*-$[Rh(LH)LCl_2]$,[11] *trans*-$[Rh(LH)\text{-}_2Cl_2]^+$,[11] $[Tc(LH)L_2]^+$,[12] and $[Pt(LH)Cl_2]$.[13]

EXPERIMENTAL

Preparations

The crystalline complex $[Ag(LH)_2(EtOH)_2](NO_3)$ was obtained from the slow evaporation of an actonitrile/aqueous ethanol solution of $AgNO_3$ (Johnson Matthey) and LH in a 1:2 ratio. Similarly, a 1:3 ratio yielded $[Ag(LH)_3]NO_3.H_2O$. Attempts to prepare the 1:1 complex resulted in the precipitation of elemental Ag. A solution containing a 1:4 Ag:LH ratio yielded the 1:3 salt and free LH.

Crystallography

Intensity data for a crystal of **1**, 0.44 × 0.30 × 0.44 mm (details for **2** follows in parentheses, 0.30 × 0.12 × 0.76 mm), were measured at room temperature on an Enraf-Nonius CAD4F diffractometer with Mo*Kα* radiation, $\lambda = 0.7107$ Å. The ω:2θ scan technique was employed to measure the intensities of 5669 reflections for **1** (7508 for **2**) such that θ_{max} was 22.5°. There was no decomposition of either crystal during its respective data collection and the data sets were corrected for Lorentz and polarization effects and for absorption with the use of an analytical procedure;[14] max. and min. transmission factors were 0.860 and 0.835, respectively (0.944 and 0.859). There were 5106 (7064) unique reflections of which 2433 (4428) satisfied the $I \geqslant 2.5\sigma(I)$ criterion of observability and were used in the subsequent analysis.

$[Ag(LH)_2(EtOH)_2](NO_3) = C_{40}H_{44}AgN_3O_5P_2$: $M_r = 816.6$, monlcinic, $P2_1/n$, $a = 10.272(4)$, $b = 16.358(2)$, $c = 23.709(3)$ Å, $\beta = 101.01(2)°$, $V = 3190.5$ Å^3, $Z = 4$, $D_c = 1.387$ g cm^{-3}, $F(000) = 1688$, $\mu = 6.01$ cm^{-1}.

$[Ag(LH)_3]NO_3.H_2O = C_{54}H_{50}AgN_4O_4P_3$: $M_r = 1019.8$, triclinic, $P\bar{1}$, $a = 11.857(2)$, $b = 21.285(2)$, $c = 11.190(4)$ Å, $\alpha = 91.77(1)$, $\beta = 104.50(2)$, $\gamma = 97.93(1)°$, $V = 2701.7$ Å^3, $Z = 2$, $D_c = 1.254$ g cm^{-3}, $F(000) = 1052$, $\mu = 4.68$ cm^{-1}.

In each case the structure was solved by interpretation of the Patterson synthesis and refined by a full-matrix least-squares procedure based on F.[14] All non-phenyl, non-H atoms were refined with anisotropic thermal parameters (except for the disordered atoms, see below) and C-bound H atoms were included in the models at their calculated positions (C-H 0.97Å). In **1** the C atoms of the second ethanol molecule were refined isotropically with a constrained C(3a)-C(4a) bond distance of 1.44(1) Å. For **2** the water molecule of crystallization was disordered over two sites (each of 50% occupancy) and these O atoms were refined isotropically. After the inclusion of a weighting scheme, $w = k/[\sigma^2(F) + |g|F^2]$, the refinements were continued until convergence; $R = 0.058$, $k = 4.1$, $g = 0.0055$, R_w 0.063 for **1**, (0.069, 1.0, 0.0099, 0.074 for **2**). The analysis of variance showed no special features and no correction was applied for extinction effects in either model. The maximum residual electron peak in the final difference map was 0.84 eÅ^{-3} for **1** (0.80 for **2**).

The scattering factors for C, H, N, O and P were those incorporated in the SHELX76 program[14] and those for Ag^+, corrected for f' and f'', were from the *International*

Tables for X-ray Crystallography.[15] Calculations were performed on a SUN4/280 computer. Fractional atomic coordinates for the two compounds are listed in Tables 1 and 2 and the numbering schemes employed are shown in Figures 1 and 2 which were drawn with ORTEP[16] at 15% probability ellipsoids. Full lists of bond lengths and angles, thermal parameters and observed and calculated structure factors are available from the author upon request.

RESULTS AND DISCUSSION

The molecular structure and crystallographic numbering scheme for $[Ag(LH)_2(EtOH)_2](NO_3)$ (**1**) is shown in Figure 1 and selected interatomic parameters are listed in Table 3. The Ag atom is coordinated by two P atoms with Ag-P(1) and Ag-P(2) being 2.433(3) and 2.439(3) Å, respectively, and P(1)-Ag-P(2) being 160.1(1)°. In addition, there are two disparate Ag-O contacts, i.e., Ag-O(1a) 2.49(1) and Ag-O(2a) 2.75(1) Å, so that the Ag atom may be thought of as being four-coordinate. The two amino groups of the aniline residue are orientated so as to lie on the same side of the molecule; however, there is no indication of a bonding interaction between the Ag atom and the amino-N atoms nor is there any interaction between the nitrate anion and the Ag atom.

To a first approximation the Ag-P bond distances and the nature of the Ag-O interactions resemble those found in the structures of $[Ag(PPh_3)_2NO_3]$ (Ag-P 2.443(1),

Table 1 Fractional atomic coordinates (× 10^5 for Ag; × 10^4 for others) for $[Ag(LH)_2(EtOH)_2](NO_3)$ (1)

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
Ag	11430(9)	6468(6)	24681(3)	C(214)	530(20)	−2251(9)	3920(6)
P(1)	702(3)	435(2)	1433(1)	C(215)	1820(16)	−2006(8)	4111(6)
P(2)	1695(3)	349(2)	3494(1)	C(216)	2162(13)	−1208(8)	4001(5)
C(111)	−112(11)	−527(7)	1205(5)	C(221)	897(8)	1055(4)	3917(3)
C(112)	−1194(12)	−769(8)	1424(5)	C(222)	375(8)	792(4)	4388(3)
N(112)	−1792(12)	−258(9)	1752(6)	C(223)	−216(8)	1354(4)	4704(3)
C(113)	−1741(14)	−1556(10)	1289(7)	C(224)	−284(8)	2178(4)	4549(3)
C(114)	−1165(17)	−2072(8)	958(7)	C(225)	238(8)	2440(4)	4078(3)
C(115)	−115(15)	−1840(9)	731(6)	C(226)	828(8)	1879(4)	3762(3)
C(116)	414(3)	−1067(8)	857(5)	C(231)	3428(8)	441(5)	3799(3)
C(121)	2151(8)	452(5)	1111(2)	C(232)	3871(8)	820(5)	4328(3)
C(122)	3341(8)	145(5)	1422(2)	C(233)	5224(8)	853(5)	4560(3)
C(123)	4475(8)	141(5)	1179(2)	C(234)	6153(8)	506(5)	4262(3)
C(124)	4420(8)	446(5)	626(2)	C(235)	5693(8)	127(5)	3733(3)
C(125)	3230(8)	753(5)	315(2)	C(236)	4339(8)	95(5)	3502(3)
C(126)	2095(8)	757(5)	558(2)	N(1)	−722(17)	3583(10)	2512(6)
C(131)	−393(7)	1210(3)	1049(3)	O(1)	−1105(13)	4254(10)	2547(6)
C(132)	−1477(7)	1012(3)	620(3)	O(2)	−1558(23)	3146(12)	2384(11)
C(133)	−2295(7)	1630(3)	343(3)	O(3)	311(18)	3358(13)	2565(10)
C(134)	−2028(7)	2445(3)	496(3)	O(1a)	1963(21)	2083(10)	2500(6)
C(135)	−944(7)	2643(3)	925(3)	C(1a)	3098(14)	2392(17)	2552(9)
C(136)	−126(7)	2025(3)	1201(3)	C(2a)	3565(20)	3183(11)	2627(7)
C(211)	1233(10)	−649(7)	3694(4)	O(2a)	−1262(11)	1393(6)	2441(4)
C(212)	−68(13)	−923(8)	3505(5)	C(3a)	−2249(22)	1304(19)	2667(11)
N(212)	−1042(11)	−435(8)	3201(5)	C(4a)	−3590(19)	1545(14)	2487(8)
C(213)	-318(16)	−1732(11)	3641(6)				

Table 2 Fractional atomic coordinates (× 10^5 for Ag; × 10^4 for others) for $[Ag(LH)_3](NO_3).H_2O$ (**2**)

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
Ag	35120(6)	22587(3)	35665(6)	C(225)	1949(7)	3706(3)	6528(6)
P(1)	2748(2)	1479(1)	4851(2)	C(226)	2629(7)	3436(3)	5858(6)
P(2)	3949(2)	3408(1)	4149(2)	C(231)	5434(6)	3574(3)	5173(7)
P(3)	4364(2)	1893(1)	1901(2)	C(232)	5757(6)	4038(3)	6154(7)
C(111)	1628(8)	1733(4)	5522(8)	C(233)	6896(6)	4126(3)	6930(7)
C(112)	726(9)	2000(5)	4780(9)	C(234)	7712(6)	3749(3)	6725(7)
N(112)	641(8)	2073(5)	3507(8)	C(235)	7389(6)	3285(3)	5745(7)
C(113)	−123(10)	2227(5)	5301(10)	C(236)	6250(6)	3197(3)	4969(7)
C(114)	−35(11)	2180(6)	6540(11)	C(311)	3366(7)	1249(4)	949(7)
C(115)	846(10)	1918(5)	7273(10)	C(312)	2134(9)	1256(5)	704(8)
C(116)	1678(8)	1686(4)	6765(8)	N(312)	1678(8)	1766(5)	1137(8)
C(121)	3914(6)	1324(3)	6149(7)	C(313)	1351(10)	722(6)	36(9)
C(122)	4832(6)	1822(3)	6621(7)	C(314)	1771(12)	234(6)	−399(10)
C(123)	5752(6)	1737(3)	7628(7)	C(315)	2969(11)	210(5)	−182(10)
C(124)	5754(6)	1154(3)	8165(7)	C(316)	3738(9)	725(5)	497(9)
C(125)	4836(6)	656(3)	7693(7)	C(321)	4663(6)	2473(3)	834(6)
C(126)	3916(6)	741(3)	6686(7)	C(322)	3931(6)	2439(3)	−363(6)
C(131)	2103(5)	700(3)	4066(6)	C(323)	4143(6)	2898(3)	−1176(6)
C(132)	964(5)	422(3)	4056(6)	C(324)	5087(6)	3391(3)	−791(6)
C(133)	493(5)	−169(3)	3425(6)	C(325)	5818(6)	3425(3)	406(6)
C(134)	1161(5)	−481(3)	2804(6)	C(326)	5607(6)	2966(3)	1218(6)
C(135)	2300(5)	−203(3)	2814(6)	C(331)	5725(6)	1580(4)	2458(5)
C(136)	2771(5)	388(3)	3445(6)	C(332)	6543(6)	1552(4)	1761(5)
C(211)	3939(9)	3896(4)	2843(9)	C(333)	7559(6)	1284(4)	2232(5)
C(212)	2966(13)	3766(6)	1810(9)	C(334)	7757(6)	1044(4)	3400(5)
N(212)	2032(9)	3287(5)	1752(10)	C(335)	6938(6)	1071(4)	4097(5)
C(213)	3003(15)	4168(7)	806(11)	C(336)	5922(6)	1340(4)	3626(5)
C(214)	3937(16)	4631(7)	891(13)	N(1)	894(20)	7684(20)	218(18)
C(215)	4920(15)	4760(6)	1883(13)	O(1)	470(23)	7549(15)	−755(26)
C(216)	4899(11)	4382(5)	2877(10)	O(2)	1032(20)	8726(13)	375(29)
C(221)	3053(7)	3779(3)	4979(6)	O(3)	1618(21)	7474(12)	772(32)
C(222)	2798(7)	4393(3)	4769(6)	Oa(1)	9204(46)	3810(28)	3095(49)
C(223)	2119(7)	4663(3)	5439(6)	Oa(2)	1213(27)	6999(16)	7400(29)
C(224)	1694(7)	4320(3)	6318(6)				

Table 3 Selected interatomic distances (Å) and bond angles (°) for $[Ag(LH)_2(EtOH)_2](NO_3)$ (**1**)

Ag-P(1)	2.433(3)	Ag-P(2)	2.439(3)
Ag-O(1a)	2.49(1)	Ag-O(2a)	2.75(1)
P(1)-C(111)	1.82(1)	P(1)-C(121)	1.798(8)
P(1)-C(131)	1.819(7)	P(2)-C(211)	1.79(1)
P(2)-C(221)	1.823(8)	P(2)-C(231)	1.795(8)
N(112)-C(112)	1.36(2)	N(212)-C(212)	1.37(2)
P(1)-Ag-P(2)	160.1(1)	P(1)-Ag-O(1a)	99.3(3)
P(1)-Ag-O(2a)	92.7(2)	P(2)-Ag-O(1a)	98.3(3)
P(2)-Ag-O(2a)	98.5(2)	O(1a)-Ag-O(2a)	83.1(6)
Ag-P(1)-C(111)	114.2(4)	Ag-P(1)-C(121)	114.6(2)
Ag-P(1)-C(131)	112.6(2)	C(111)-P(1)-C(121)	105.0(5)
C(111)-P(1)-C(131)	104.5(4)	C(121)-P(1)-C(131)	105.0(3)
Ag-P(2)-C(211)	115.1(3)	Ag-P(2)-C(221)	112.3(3)
Ag-P(2)-C(231)	114.1(3)	C(211)-P(2)-C(221)	105.2(4)
C(211)-P(2)-C(231)	105.2(4)	C(221)-P(2)-C(231)	104.0(3)
Ag-O(1a)-C(1a)	133(2)	Ag-O(2a)-C(3a)	138(1)

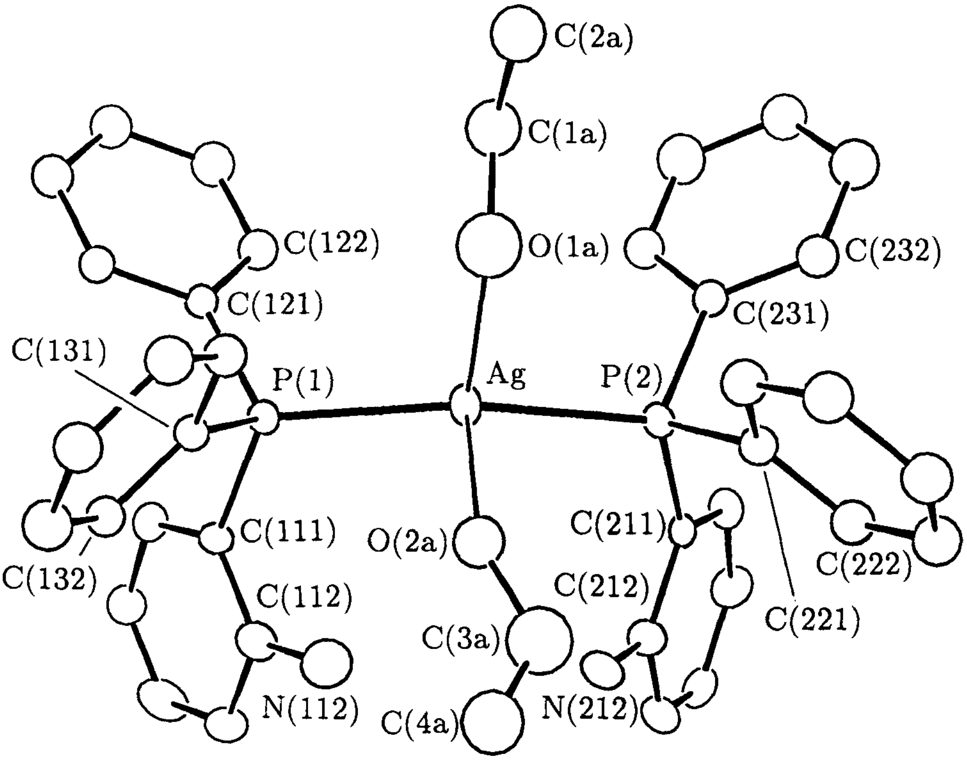

Figure 1 The molecular structure of the cation in $[Ag(LH)_2(EtOH)_2](NO_3)$ (1) showing the crystallographic numbering scheme employed.

2.440(1), Ag-O 2.464(4), 2.649(4) Å, P-Ag-P 138.21(5)°),[17] $[Ag(PPh_3)_2NO_3].C_6H_6$ (Ag-P 2.435(1), 2.416(1), Ag-O 2.463(2), 2.572(2) Å, P-Ag-P 139.4(1)°)[18] and $[Ag(P^chex_3)_2NO_3]$ (Ag-P 2.440(3), 2.445(3), Ag-O 2.45(1), 2.73(1) Å and P-Ag-P 139.04(9)°).[19] The major difference between these latter structures is found in the magnitude of the P-Ag-P angle which is *ca* 140°, i.e., 20° less than that found in **1**. This difference may simply reflect the less sterically demanding positions occupied by the two ethanol molecules in **1** in contrast to the other three adducts in which the O atoms, derived from the nitrate anions, effectively occupy one position and therefore exert greater steric pressure in the molecule, contracting the P-Ag-P angle. In this context it is interesting to note that in two salts $[Ag(Pmesityl_3)_2][PF_6]$[20] and $\{Ag[P(NMe_2)_3]\}[BF_4]$,[21] in which the anion does not coordinate the Ag atom, the P-Ag-P angles are 179.4(5) and 166.9(1)°, respectively.

The molecular structure of $[Ag(LH)_3](NO_3).H_2O$ (**2**) is shown in Figure 2 showing the crystallographic numbering scheme employed and Table 4 lists important interatomic parameters. The Ag atom is coordinated by three P atoms which form different Ag-P bond distances, i.e., Ag-P(1) 2.455(2), Ag-P(2) 2.462(2) and Ag-P(3) 2.484(2) Å. The three amino groups lie on the same side of the molecule so that the cation has approximate three-fold symmetry; as for **1**, no evidence was found for Ag...amino-N interactions with Ag...N(112), Ag...N(212) and Ag...N(312) being 3.356(9),

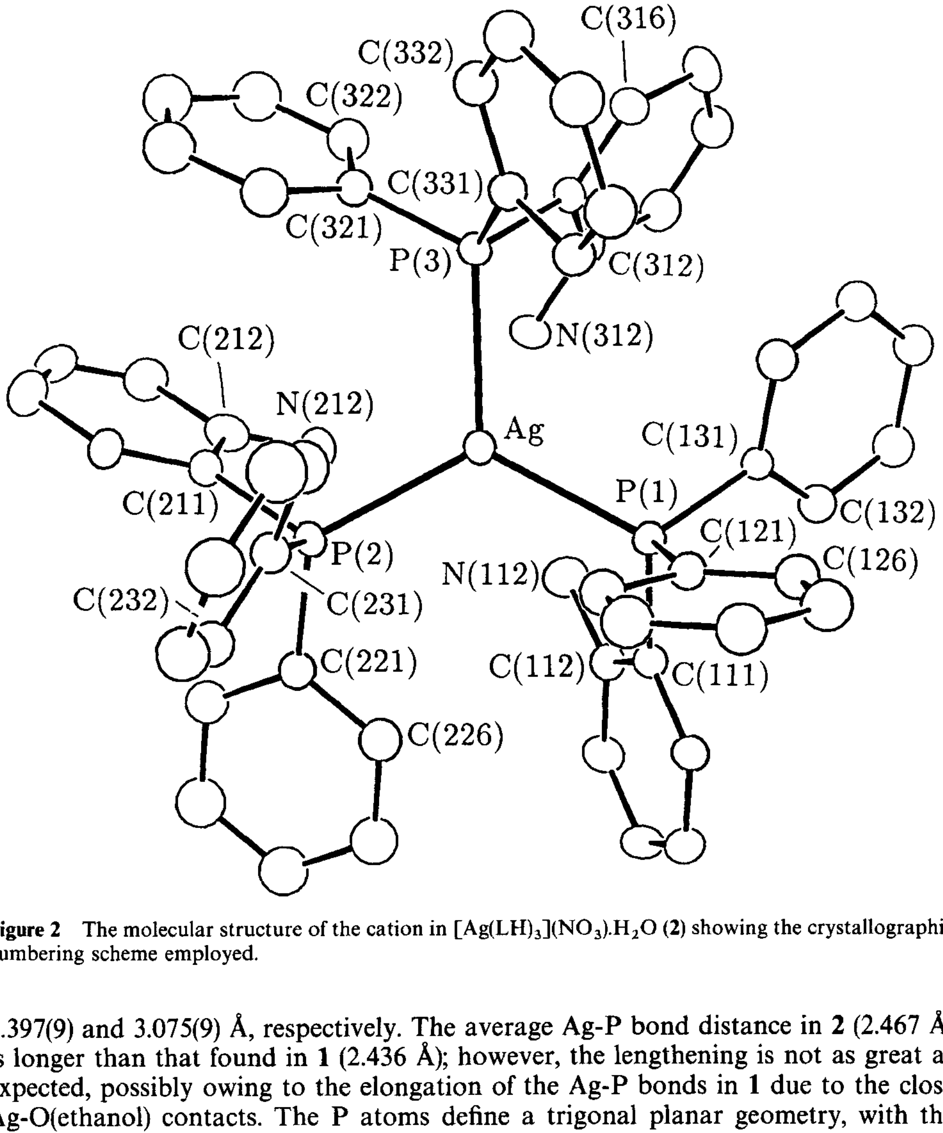

Figure 2 The molecular structure of the cation in $[Ag(LH)_3](NO_3).H_2O$ (**2**) showing the crystallographic numbering scheme employed.

3.397(9) and 3.075(9) Å, respectively. The average Ag-P bond distance in **2** (2.467 Å) is longer than that found in **1** (2.436 Å); however, the lengthening is not as great as expected, possibly owing to the elongation of the Ag-P bonds in **1** due to the close Ag-O(ethanol) contacts. The P atoms define a trigonal planar geometry, with the three P-Ag-P angles being 122.9(1), 119.7(1) and 115.7(1)° (sum = 358.3°), and the Ag atom lies 0.192(1) Å above this plane. There are no intermolecular contacts between the Ag atom and the nitrate group or solvent water molecule of crystallization less than 4.0 Å.

There have been several other crystal structure determinations of triphosphine adducts of Ag. However, each of these feature a close contact (or contacts) between the Ag atom and an atom of the anion, i.e., $[Ag(PPh_3)_3X]X$ = Cl (Ag-Cl 2.552(1) Å),[22] I (Ag-I 2.855(1) Å),[23] BF_4(Ag-F 2.82(1) Å)[23] and NO_3 (Ag-O 2.684(6) and 2.775(6) Å);[17] and $[Ag(PPh_2{}^cPent)_3BF_4]$ (Ag-F 2.54(2) Å).[24] In **2**, the absence of a close contact between the Ag atom and the nitrate anion indicates that this structure is a rare example of a triphosphine adduct of Ag containing a truly isolated AgP_3 core.

Table 4 Selected interatomic distances (Å) and bond angles (°) for $[Ag(LH)_3](NO_3).H_2O$ (**2**)

Ag-P(1)	2.455(2)	Ag-P(2)	2.462(2)
Ag-P(3)	2.484(2)	P(1)-C(111)	1.814(9)
P(1)-C(121)	1.811(7)	P(1)-C(131)	1.824(6)
P(2)-C(211)	1.819(9)	P(2)-C(221)	1.814(7)
P(2)-C(231)	1.825(8)	P(3)-C(311)	1.802(8)
P(3)-C(321)	1.805(8)	P(3)-C(331)	1.803(7)
N(112)-C(112)	1.42(1)	N(212)-C(212)	1.39(2)
N(312)-C(312)	1.40(1)		
P(1)-Ag-P(2)	122.9(1)	P(1)-Ag-P(3)	119.7(1)
P(2)-Ag-P(3)	115.7(1)	Ag-P(1)-C(111)	114.0(3)
Ag-P(1)-C(121)	110.8(2)	Ag-P(1)-C(131)	115.1(2)
C(111)-P(1)-C(121)	105.6(4)	C(111)-P(1)-C(131)	105.5(3)
C(121)-P(1)-C(131)	105.0(3)	Ag-P(2)-C(211)	113.6(3)
Ag-P(2)-C(221)	120.3(2)	Ag-P(2)-C(231)	107.8(2)
C(211)-P(2)-C(221)	103.2(4)	C(211)-P(2)-C(231)	106.7(4)
C(211)-P(2)-C(231)	104.2(3)	Ag-P(3)-C(311)	110.0(3)
Ag-P(3)-C(321)	116.5(3)	Ag-P(3)-C(331)	114.0(2)
C(311)-P(3)-C(321)	104.9(3)	C(311)-P(3)-C(331)	105.1(4)
C(321)-P(3)-C(331)	105.3(3)		

Acknowledgments

Dr P.A. Duckworth is thanked for the gift of the phosphine ligand used in this study and for helpful discussion. The Australian Research Council is thanked for support of the crystallographic facility.

References

1. D.R. Haynes and M.W. Whitehouse, in K.D. Rainsford and G.P. Velo (eds), *New Developments in Antirheumatic Therapy*, (Kluwer, Dordrecht, 1989), Ch. 8.
2. B.M. Sutton, E. McGusty, D.T. Walz and M.J. DiMartino, *J. Med. Chem.*, **15**, 1095 (1972).
3. B.M. Sutton, *Gold Bull.*, **19**, 15 (1986).
4. S.J. Berners-Price, R.K. Johnson, A.J. Giovenella, L.F. Faucette, C.K. Mirabelli and P.J. Sadler, *J. Bioinorg. Chem.*, **33**, 285 (1988).
5. S.J. Berners-Price, R.K. Johnson, C.K. Mirabelli, L.F. Faucette, F.L. McCabe ad P.J. Sadler, *Inorg. Chem.*, **26**, 3383 (1987).
6. C.S.W. Harker and E.R.T. Tiekink, *J. Coord. Chem.*, **21**, 287 (1990).
7. P.A. Bates and J.M. Waters, *Inorg. Chim. Acta.*, **81**, 151 (1984).
8. S.J. Berners-Price, M.A. Mazid and P.J. Sadler, *J. Chem. Soc., Dalton Trans.*, 969 (1984).
9. C.S.W. Harker, E.R.T. Tiekink and M.W. Whitehouse, *Inorg. Chim. Acta.*, **181**, 23 (1991).
10. M.K. Cooper, J.M. Downes, H.J. Goodwin and M. McPartlin, *Inorg. Chim. Acta.*, **76**, L157 (1983).
11. G.J. Organ, M.K. Cooper, K. Henrick and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 2377 (1984).
12. F. Refosco, C. Bolzati, A. Moresco, G. Bandoli, A. Dolmella, U. Mazzi and M. Nicolini, *J. Chem. Soc., Dalton Trans.*, 3043 (1991).
13. G.B. Deacon, P.A. Jackson, K.T. Nelson and E.R.T. Tiekink, *Acta Cryst.*, **C47**, 2090 (1991).
14. G.M. Sheldrick, "SHELX76. Program for crystal structure determination", (Cambridge University, England, 1976).
15. J.A. Ibers and W.C. Hamilton, Editors, "International Tables for X-ray Crystallography", Vol. IV, pp. 99, 149 (Birmingham, Kynoch Press, 1974).
16. C.K. Johnson, ORTEPII, *Report 5138, Oak-Ridge National Laboratory*, Tennessee (1976).
17. P.F. Barron, J.C. Dyason, P.C. Healy, L.M. Engelhardt, B.W. Skelton and A.H. White, *J. Chem. Soc., Dalton Trans.*, 1965 (1986).
18. C.S.W. Harker and E.R.T. Tiekink, *Acta Cryst.*, **45**, 1815 (1989).

19. M. Camalli and F. Caruso, *Inorg. Chim. Acta*, **144**, 205 (1988).
20. E.C. Alyea, G. Ferguson and A. Somogyvari, *Inorg. Chem.*, **21**, 1369 (1982).
21. S.M. Socol, R.A. Jacobson and J.G. Verkade, *Inorg. Chem.*, **23**, 88 (1984).
22. A. Cassel, *Acta Cryst.*, **B37**, 229 (1981).
23. M. Camalli and F. Caruso, *Inorg. Chim. Acta*, **127**, 209 (1987).
24. A. Baiada, F.H. Jardine and R.D. Willett, *Inorg. Chem.*, **29**, 4805 (1990).