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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF TWO ARSINE COMPLEXES OF SILVER(I)

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Summary

The syntheses and X-ray crystal structures of $Ag(AsPh_3)_3Cl \cdot 0.5CH_3COCH_3$ (**1**) and of $(AgNO_3)_2(Ph_2AsCH_2CH_2AsPh_2)$ (**2**) are described. The crystal structure of **1** contains discrete monomeric $Ag(AsPh_3)_3Cl$ units in which Ag is tetrahedrally surrounded by three As atoms and one Cl atom, along with solvating acetone molecules. Compound **2** exists in the crystalline form as polymeric layers, since the diarsine ligand bridges the two independent silver atoms to form a dimer and the dimers are held together in layers through connecting nitrate groups. Carbon atoms of adjacent phenyl rings complete the environment of both the silver atoms and aid in binding the molecules together.

Introduction

In a research program on the coordinating behaviour of ligands containing P or As we have recently investigated the syntheses and structures of tin adducts [1] and silver-tin complex salts [2,3] with phosphines and arsines. We now report on the preparation and the crystal and molecular structure of two silver complexes of formula $Ag(AsPh_3)_3Cl \cdot 0.5CH_3COCH_3$ (**1**) and $(AgNO_3)_2(Ph_2AsCH_2CH_2AsPh_2)$ (**2**), obtained respectively from the reaction of silver chloride with triphenylarsine and the reaction of silver nitrate with 1,2-bis(diphenylarsino)ethane.

Experimental

Preparation

$Ag(AsPh_3)_3Cl \cdot 0.5CH_3COCH_3$. Finely powdered silver chloride was added to $AsPh_3$ (in slight excess over a 1/3 molar ratio) dissolved in acetone/acetonitrile mixture. The resulting suspension was stirred at room temperature and allowed to stand overnight. After some days a white crystalline product was formed. The complex can be also obtained by treating $Ag(AsPh_3)_3NO_3$ dissolved in ethanol/acetone with 0.02 *N* aqueous hydrogen chloride.

$(AgNO_3)_2(Ph_2AsCH_2CH_2AsPh_2)$. Silver nitrate dissolved in a mixture of acetonitrile and acetone was added at room temperature to an acetone solution of 1,2-bis(diphenylarsino)ethane (2/1 molar ratio). White crystals began to form upon slow evaporation of the solvents. The product slowly blackens upon prolonged exposure to light.

X-ray data collection

For both compounds preliminary cell constants, crystal symmetry, and space group were obtained from oscillation and Weissenberg photographs taken with Cu-K_α radiation. Precise unit-cell parameters with estimated standard deviations were determined by a least-squares refinement using the θ angles for 18–20 reflections carefully centered on a three-circle Siemens AED computer-controlled diffractometer.

Intensity data were collected at room temperature on this diffractometer using the moving counter-moving crystal scan-technique with Cu-K_α radiation for **1** and Mo-K_α radiation for **2**.

A summary of relevant crystallographic data with various details of the data collection and structure refinement is given in Table 1 for the two compounds. For compound **1** 3564 unique reflections, out of a total of 8025 measured, were

TABLE 1

CRYSTALLOGRAPHIC DATA AND DETAILS OF INTENSITY DATA COLLECTION AND STRUCTURE REFINEMENT

Compound	$Ag(AsPh_3)_3Cl \cdot 0.5CH_3COCH_3$	$(AgNO_3)_2(Ph_2AsCH_2CH_2AsPh_2)$
Formula	$C_{55.5}H_{48}AgAs_3ClO_{0.5}$	$C_{26}H_{24}Ag_2As_2N_2O_6$
M.W.	1091.08	826.06
Crystal size (mm)	0.11 × 0.18 × 0.35	0.06 × 0.11 × 0.22
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	13.438(2)	19.942(20)
b (Å)	14.055(3)	8.159(5)
c (Å)	14.166(3)	18.065(23)
α (°)	95.45(2)	90
β (°)	87.01(2)	109.8(1)
γ (°)	103.92(1)	90
U (Å^3)	2584(1)	2766(5)
Z	2	4
D_c (g cm^{-3})	1.402	1.984
$F(000)$	1096	1608
Radiation, λ (Å)	Cu-K_α, 1.54178	Mo-K_α, 0.71069
μ (cm^{-1})	60.8	38.1
2θ-limits (°)	5.0–120.0	5.0–48.0
Scan speed (° s^{-1})	0.2–0.05	0.2–0.05
Scan width d (°)	$1.20 + 0.33 \tan\theta$	$1.20 + 0.33\tan\theta$
Scan type	$\theta - 2\theta$	$\theta - 2\theta$
Total reflections measured	8025	4556
Total unique reflections	8025	4272
Total observed reflections	3564	1236
Criterion for observation	$I > 3\sigma(I)$	$I > 2\sigma(I)$
No. of parameters varied	548	173
Final R	0.0545	0.0645

considered observed, having $I > 3\sigma(I)$. For compound **2** a total of 4272 unique reflections was measured, and of these only 1236 reflections were judged to be observed on the criterion $I > 2\sigma(I)$. Two reflections for **1** and one reflection for **2** were chosen as standards and checked periodically for any indication of decomposition. No significant variation was found for **2**, while a ~ 10% decrease in intensity was observed during the date collection for **1** and this effect was corrected by scaling the reflections with respect to the standards. The data were corrected for background and Lorentz and polarization effects, but not for extinction or absorption.

Structure determination and refinement

In both structures a three-dimensional Patterson map revealed the positional parameters of the silver atom, and from a subsequent Fourier synthesis phased on the phases of the Ag contributions, the As atoms were located. The remaining non-hydrogen atoms were found in a series of alternating structure factors calculations and difference Fourier maps.

TABLE 2

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) FOR $Ag(AsPh_3)_3Cl \cdot 0.5CH_3COCH_3$

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
Ag	2555(1)	6822(1)	2691(1)	C(28)	1447(13)	4687(13)	6374(12)
As(1)	2369(1)	5027(1)	1916(1)	C(29)	2203(11)	5446(13)	6777(11)
As(2)	3292(1)	7045(1)	4408(1)	C(30)	2749(10)	6178(11)	6198(9)
As(3)	3525(1)	8183(1)	1612(1)	C(31)	3190(11)	8225(9)	5199(9)
Cl	812(3)	7186(4)	2964(4)	C(32)	4022(13)	8747(11)	5779(10)
C(1)	3678(10)	4671(8)	1759(10)	C(33)	3856(14)	9521(12)	6388(13)
C(2)	3983(13)	4185(12)	937(10)	C(34)	2976(15)	9855(12)	6427(12)
C(3)	4987(14)	4002(14)	848(12)	C(35)	2186(13)	9361(12)	5841(14)
C(4)	5665(12)	4313(12)	1596(12)	C(36)	2309(11)	8532(11)	5200(11)
C(5)	5342(12)	4808(11)	2429(12)	C(37)	4989(9)	8240(9)	1384(8)
C(6)	4365(11)	5007(9)	2507(9)	C(38)	5302(10)	7406(10)	1502(10)
C(7)	1788(9)	4649(9)	683(9)	C(39)	6329(13)	7386(12)	1320(11)
C(8)	1428(10)	3711(10)	346(10)	C(40)	7044(11)	8253(13)	1108(11)
C(9)	913(11)	3487(13)	−530(11)	C(41)	6724(11)	9100(12)	993(11)
C(10)	829(12)	4242(16)	−1049(11)	C(42)	5710(11)	9096(9)	1170(9)
C(11)	1210(13)	5234(14)	−722(11)	C(43)	3537(9)	9545(9)	2065(9)
C(12)	1703(10)	5447(10)	169(10)	C(44)	3712(10)	10293(10)	1521(11)
C(13)	1570(10)	3942(8)	2562(9)	C(45)	3752(12)	11253(11)	1917(14)
C(14)	559(11)	3966(10)	2809(10)	C(46)	3605(12)	11431(11)	2870(14)
C(15)	−71(11)	3229(12)	3302(11)	C(47)	3411(12)	10681(13)	3422(11)
C(16)	300(13)	2492(12)	3596(12)	C(48)	3384(10)	9719(11)	3049(10)
C(17)	1343(14)	2490(12)	3352(14)	C(49)	3025(11)	8134(9)	325(8)
C(18)	1956(12)	3233(11)	2857(11)	C(50)	3710(11)	8142(9)	−463(9)
C(19)	4724(10)	7005(9)	4528(9)	C(51)	3307(14)	8104(10)	−1385(9)
C(20)	5452(12)	7623(11)	3997(10)	C(52)	2236(14)	8058(11)	−1479(12)
C(21)	6473(13)	7585(13)	4013(13)	C(53)	1591(12)	8068(12)	−653(12)
C(22)	6778(12)	6946(12)	4526(13)	C(54)	2003(11)	8077(11)	234(11)
C(23)	6087(13)	6352(12)	5042(12)	O	−225(21)	−809(21)	679(22)
C(24)	5016(11)	6357(10)	5080(10)	C(55)	109(36)	−132(36)	1503(35)
C(25)	2544(10)	6077(9)	5235(8)	C(56)	−49(32)	−372(33)	2462(33)
C(26)	1806(10)	5326(9)	4827(10)	C(57)	893(35)	447(32)	1042(33)
C(27)	1230(12)	4608(10)	5401(12)				

Both the structures were refined by full-matrix least-squares procedures. During the refinement of compound **1** the presence of half a molecule of solvated acetone per asymmetric unit was established, this group being found to be statistically disordered over two positions about a center of symmetry. The atoms of **1** were allowed to vibrate anisotropically except those belonging to the solvent molecule. No constraint to the phenyl rings was applied. The reliability indices converged at $R = 0.0545$ and $R' = 0.0583$. With regard to compound **2**, anisotropic thermal parameters were determined only for Ag and As. Extending anisotropic refinement to the light atoms resulted in convergence difficulties with thermal quadratic form of almost half of these atoms becoming non positive definite. After 21 bad reflections in the data set were rejected, refinement was continued and converged to discrepancy factors of $R = 0.0645$ and $R' = 0.0663$.

In neither case was an attempt made to find the hydrogen atoms. The function minimized during the least-squares refinement was $\Sigma w|\Delta F^2|$ and the reflections were weighted according to the expression $w = k/\sigma^2(F_0) + \text{abs}(g)F_0^2$, based on counting statistics. In both structures the final difference Fourier map was essentially featureless. Complex neutral-atom scattering factors were taken from International Tables for X-ray Crystallography [4] as were corrections for the real and imaginary component of the anomalous dispersion of Ag and As. All computations were performed using the SHELX-76 system of crystallographic programs [5] on the CDC Cyber 76 computer of CINECA (Casalecchio, Bologna), with financial support from University of Parma.

Tables 2 and 3 give the final atomic coordinates for **1** and **2**, with estimated standard deviations in the last digits in parentheses. Tables of observed and calculated structure factors and thermal parameters are available from the authors.

TABLE 3

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) FOR $(AgNO_3)_2(Ph_2AsCH_2CH_2AsPh_2)$

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Ag(1)	2571(2)	2970(4)	1537(2)	C(8)	4099(16)	−304(37)	1841(17)
Ag(2)	2637(1)	−3421(4)	−1473(2)	C(9)	4699(18)	−1224(43)	2230(21)
As(1)	3263(2)	1998(3)	696(2)	C(10)	5234(17)	−1180(42)	1971(20)
As(2)	1961(2)	−2405(4)	−664(2)	C(11)	5263(16)	−176(37)	1335(18)
O(1)	2826(17)	4847(39)	2662(18)	C(12)	4692(17)	762(39)	970(19)
O(2)	3276(15)	7335(38)	2776(18)	C(13)	2754(13)	496(31)	−146(15)
O(3)	3096(15)	6087(36)	1743(20)	C(14)	2449(13)	−846(31)	200(15)
O(4)	2450(12)	747(27)	2549(13)	C(15)	1167(17)	−1074(40)	−1244(20)
O(5)	1690(14)	−1265(36)	2146(16)	C(16)	1258(15)	−76(36)	−1845(16)
O(6)	1680(16)	793(38)	1454(20)	C(17)	720(20)	1001(45)	−2205(22)
N(1)	2988(18)	5920(48)	2406(22)	C(18)	96(16)	1005(37)	−2074(18)
N(2)	1956(19)	92(46)	2114(22)	C(19)	−11(18)	48(45)	−1526(21)
C(1)	3620(12)	3632(31)	156(14)	C(20)	513(18)	−955(41)	−1083(20)
C(2)	3903(14)	5069(33)	553(16)	C(21)	1555(16)	−4000(39)	−166(19)
C(3)	4148(17)	6299(42)	202(20)	C(22)	1427(18)	−3690(43)	492(22)
C(4)	4133(16)	6073(41)	−589(19)	C(23)	1097(20)	−4845(51)	842(23)
C(5)	3829(14)	4707(34)	−972(16)	C(24)	967(24)	−6388(61)	440(30)
C(6)	3595(13)	3437(31)	−601(15)	C(25)	1090(24)	−6661(57)	−201(30)
C(7)	4098(14)	744(31)	1209(26)	C(26)	1381(20)	−5496(51)	−518(23)

Selected bond distances and angles are listed in Tables 4 and 5, for **1** and **2**, respectively.

Results and discussion

$Ag(AsPh_3)_3Cl \cdot 0.5CH_3COCH_3$. The structure of this compound can be considered as made up of [$Ag(AsPh_3)_3Cl$] units with acetone molecules stabilizing the crystal packing. As can clearly be seen from Fig. 1, the coordination polyhedron about the silver atom is a slightly distorted tetrahedron consisting of three arsenic atoms of the triphenylarsine molecules and one chlorine atom. An axis passing through the Ag–Cl bond is of almost C_3 symmetry.

TABLE 4

SELECTED BOND DISTANCES (Å) AND ANGLES (°) IN $Ag(AsPh_3)_3Cl$

Ag–As(1)	2.614(2)	As(1)–C(1)	1.94(1)	As(2)–C(31)	1.94(1)
Ag–As(2)	2.637(2)	As(1)–C(7)	1.93(1)	As(3)–C(37)	1.96(1)
Ag–As(3)	2.616(2)	As(1)–C(13)	1.92(1)	As(3)–C(43)	1.96(1)
Ag–Cl	2.518(5)	As(2)–C(19)	1.96(1)	As(3)–C(49)	1.96(1)
		As(2)–C(25)	1.94(1)		
As(1)–Ag–As(2)	111.82(8)	Ag–As(1)–C(13)	119.6(4)	C(1)–As(1)–C(13)	100.9(5)
As(1)–Ag–As(3)	114.07(8)	Ag–As(2)–C(19)	118.1(4)	C(7)–As(1)–C(13)	98.1(5)
As(2)–Ag–As(3)	112.97(8)	Ag–As(2)–C(25)	113.5(4)	C(19)–As(2)–C(25)	103.8(5)
As(1)–Ag–Cl	109.95(13)	Ag–As(2)–C(31)	117.3(4)	C(19)–As(2)–C(31)	102.9(5)
As(2)–Ag–Cl	103.68(14)	Ag–As(3)–C(37)	115.1(4)	C(25)–As(2)–C(31)	98.5(5)
As(3)–Ag–Cl	103.44(14)	Ag–As(3)–C(43)	116.7(4)	C(37)–As(3)–C(43)	102.2(5)
Ag–As(1)–C(1)	112.0(4)	Ag–As(3)–C(49)	117.3(4)	C(37)–As(3)–C(49)	102.9(5)
Ag–As(1)–C(7)	120.3(4)	C(1)–As(1)–C(7)	102.9(6)	C(43)–As(3)–C(49)	100.4(5)

TABLE 5

SELECTED BOND DISTANCES (Å) AND ANGLES (°) IN $(AgNO_3)_2(Ph_2AsCH_2CH_2AsPh_2)$[a]

Ag(1)–As(1)	2.502(6)	Ag(2)–As(2)	2.444(6)	As(1)–C(1)	1.93(3)
Ag(1)–O(1)	2.46(3)	Ag(2)–O(2^{i})	2.33(3)	As(1)–C(7)	1.91(2)
Ag(1)–O(3)	2.73(3)	Ag(2)–O(4^{ii})	2.53(2)	As(1)–C(13)	1.95(2)
Ag(1)–O(4)	2.64(2)	Ag(2)–O(5^{ii})	2.58(2)	As(2)–C(14)	1.99(2)
Ag(1)–O(6)	2.48(3)	C(13)–C(14)	1.49(4)	As(2)–C(15)	1.91(3)
				As(2)–C(21)	1.91(3)
As(1)–Ag(1)–O(1)	134.2(9)	As(2)–Ag(2)–O(2^{i})	137.8(8)	C(1)–As(1)–C(7)	101.9(12)
As(1)–Ag(1)–O(3)	96.5(7)	As(2)–Ag(2)–O(4^{ii})	133.7(6)	C(1)–As(1)–C(13)	102.9(11)
As(1)–Ag(1)–O(4)	113.6(5)	As(2)–Ag(2)–O(5^{ii})	103.9(7)	C(7)–As(1)–C(13)	100.4(11)
As(1)–Ag(1)–O(6)	105.5(8)	O(2^{i})–Ag(2)–O(4^{ii})	81.9(9)	Ag(2)–As(2)–C(14)	117.6(8)
O(1)–Ag(1)–O(3)	49.0(10)	O(2^{i})–Ag(2)–O(5^{ii})	80.8(10)	Ag(2)–As(2)–C(15)	112.8(11)
O(1)–Ag(1)–O(4)	84.1(9)	O(4^{ii})–Ag(2)–O(5^{ii})	50.6(8)	Ag(2)–As(2)–C(21)	117.2(10)
O(1)–Ag(1)–O(6)	116.1(11)	Ag(1)–As(1)–C(1)	117.6(8)	C(14)–As(2)–C(15)	99.2(13)
O(3)–Ag(1)–O(4)	131.8(9)	Ag(1)–As(1)–C(7)	116.5(9)	C(14)–As(2)–C(21)	103.8(12)
O(3)–Ag(1)–O(6)	155.5(10)	Ag(1)–As(1)–C(13)	115.1(9)	C(15)–As(2)–C(21)	103.9(14)
O(4)–Ag(1)–O(6)	47.1(9)				

[a] $i = x, \frac{1}{2} - y, z - \frac{1}{2}$ $ii = x, -\frac{1}{2} - y, z - \frac{1}{2}$.

The Ag–As bond lengths, with values of 2.614(2), 2.637(2), and 2.616(2) Å, are nearly equal, and the mean value of 2.622(2) Å agrees well with the mean value of 2.634(2) Å found in the closely related $Ag(AsPh_3)_3NO_3$ [2]. The Ag–Cl bond length of 2.518(5) Å is only a little shorther than the value of 2.552(1) Å found in $Ag(PPh_3)_3Cl$ [6]. The As–Ag–Cl angles are close to or less than the tetrahedral angle, while the As–Ag–As angles are significantly larger.

Within each $AsPh_3$ grouping the As atoms lie in approximate tetrahedral environment among one Ag and three C atoms. The bond angles at As are fully consistent with the usual tendency for C–As–C angles in arsine complexes to be smaller than 109.5° and Ag–As–C angles to be larger. The As–C bond distances average 1.94(1) Å (1.92(1) to 1.96(1) Å), which is a normal value. All the phenyl rings are planar within experimental error, with no significant departure from the expected structural parameters. The displacements of the attached As atoms from the respective planes are $\leqslant 0.15$ Å.

The crystal packing of the molecules involves only Van der Waals forces.

The infrared spectrum of the complex is characterized by the vibrational bands of triphenylarsine, which are very similar to those observed for the free ligand. In fact with the exception of a strong band at 1380 cm^{-1} (only a weak absorption is present at 1375 cm^{-1} in the free ligand spectrum) attributable to the ring stretching vibrations, only small shifts involving some ν(As–C) bands in the 1000 and 400 cm^{-1} regions are observed [7].

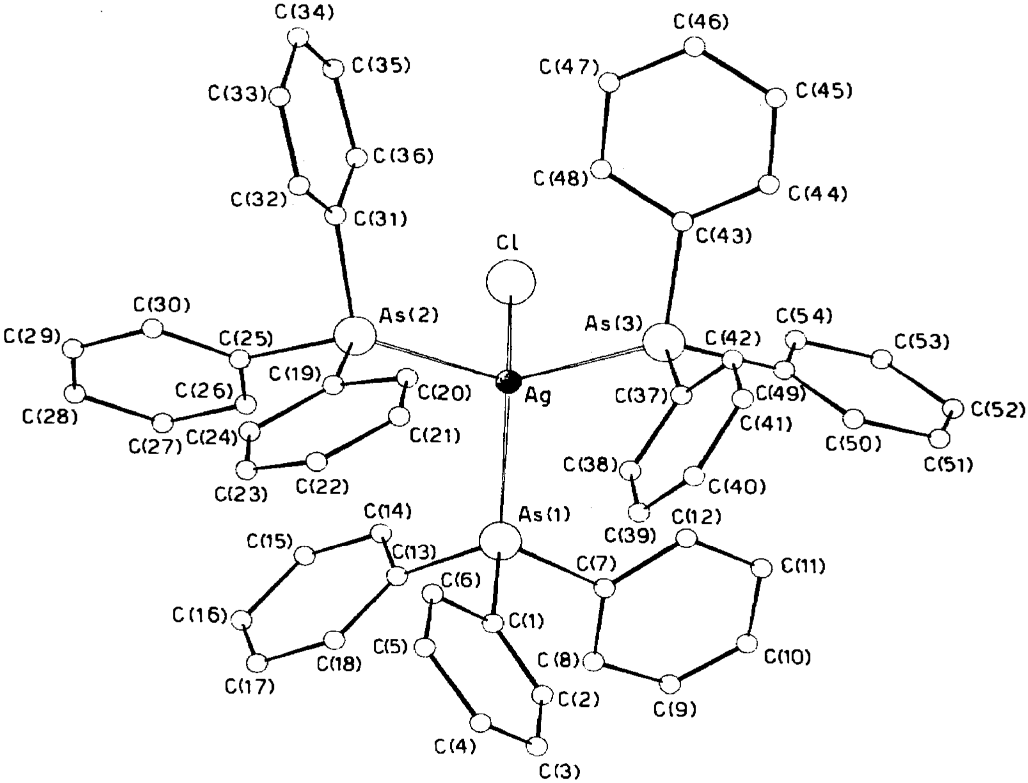

Fig. 1. Perspective view of $Ag(AsPh_3)_3Cl$ showing the atom-labeling scheme.

$(AgNO_3)_2(Ph_2AsCH_2CH_2AsPh_2)$. As shown in Fig. 2 the diarsine molecule acts as a bridging group linking the two independent silver atoms together to form a dimer. Although not required of the molecule in the crystal, the dimer has approximate $\bar{1}$ symmetry, with a pseudo center of inversion at the middle of the CH_2–CH_2 bond. The bridging action of both the nitrate ions, with all their oxygens participating in metal bonding, leads to formation of polymeric layers parallel to the *bc* plane and intersecting the *a* axis at the points 1/4 and 3/4. This can be seen in Fig. 3, which illustrates the layer at 1/4. The presence of pseudo inversion centers at the points 1/4 and 3/4 has the consequence that adjacent layers are stacked exactly above each other with no horizontal offset. This structure is undoubtedly somewhat peculiar in that the unit cell contents repeat almost exactly at intervals of 1/2 *a*; indeed, the pseudo symmetry of the $Ag_2(Ph_2AsCH_2CH_2AsPh_2)$ unit (the two nitrate groups are not considered) is remarkable. The X-ray data correspondingly looked very peculiar, with an enormously strong 200 reflection as shown by a Weissenberg photograph (this reflection was not accessible on the diffractometer

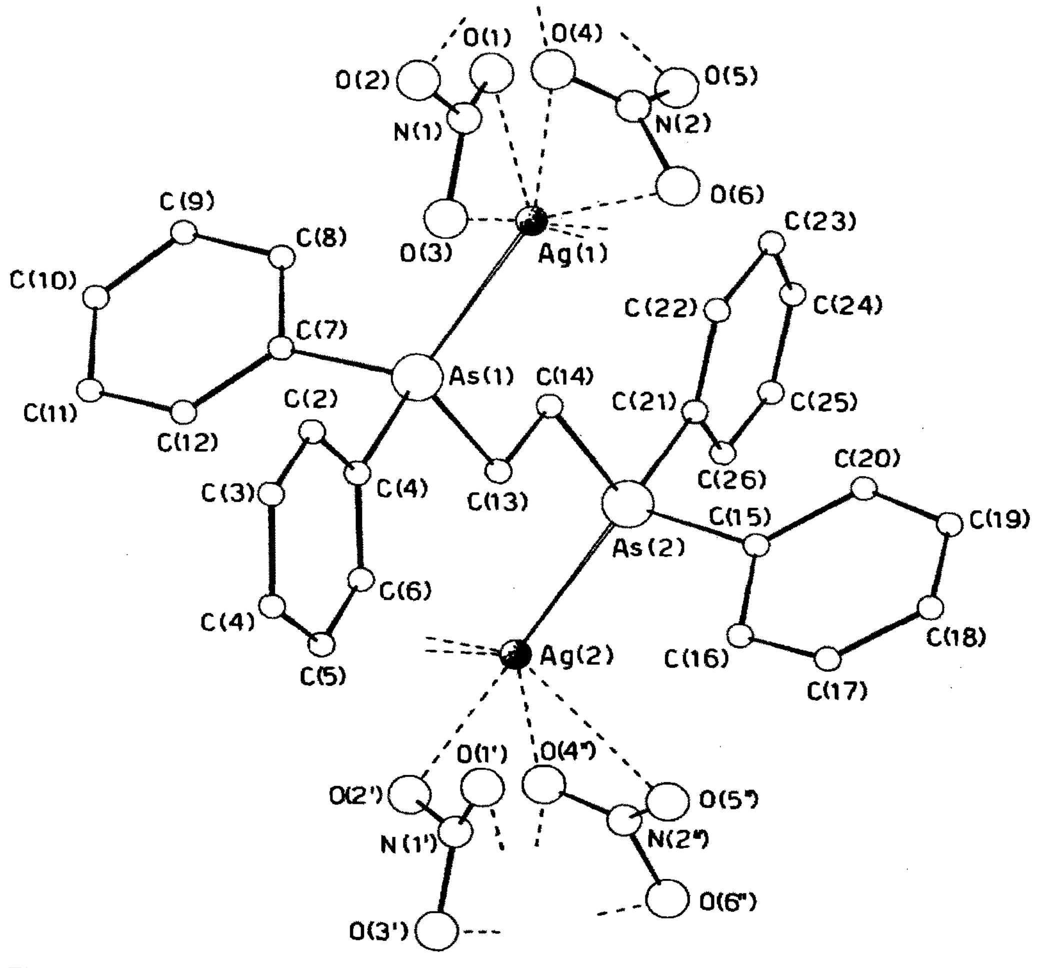

Fig. 2. Perspective view of $(AgNO_3)_2(Ph_2AsCH_2CH_2AsPh_2)$ showing the atom-labeling scheme. The diagram emphasizes the bridging action of the diarsine ligand and the environment of the silver atoms.

having $\theta < 2.5°$) and with the reflections with h odd, although accessible in a fair number, rather weak compared to those with h even. The layers are held together only by Van der Waals forces.

Both the coordination polyhedra about the two silver atoms are difficult to describe in terms of bonding geometry as there are marked distortions from ideal geometries. Ag(1) is bonded to As(1) and to four O atoms from the two independent bidentate nitrate groups, the angle range being 47.1(9)–155.5(10)°. In addition Ag(1) makes two very loose contacts with a neighbouring phenyl ring of the diarsine molecule at $x, y+1, z$ (Ag(1) · · · C(23) 3.30(4); Ag(1) · · · C(24) 3.18(4) Å). Ag(2) is surrounded by As(2) and three O atoms belonging to two different nitrates, symmetry related to those bonded to Ag(1); the angles at Ag(2) vary from 50.6(8) to 137.8(8)°. The environment of Ag(2) is completed by two carbon atoms, C(4) and C(5), from a phenyl ring of an adjacent diarsine molecule at $x, y-1, z$; these atoms come within the coordination sphere of the metal with distances of 2.90(3) and

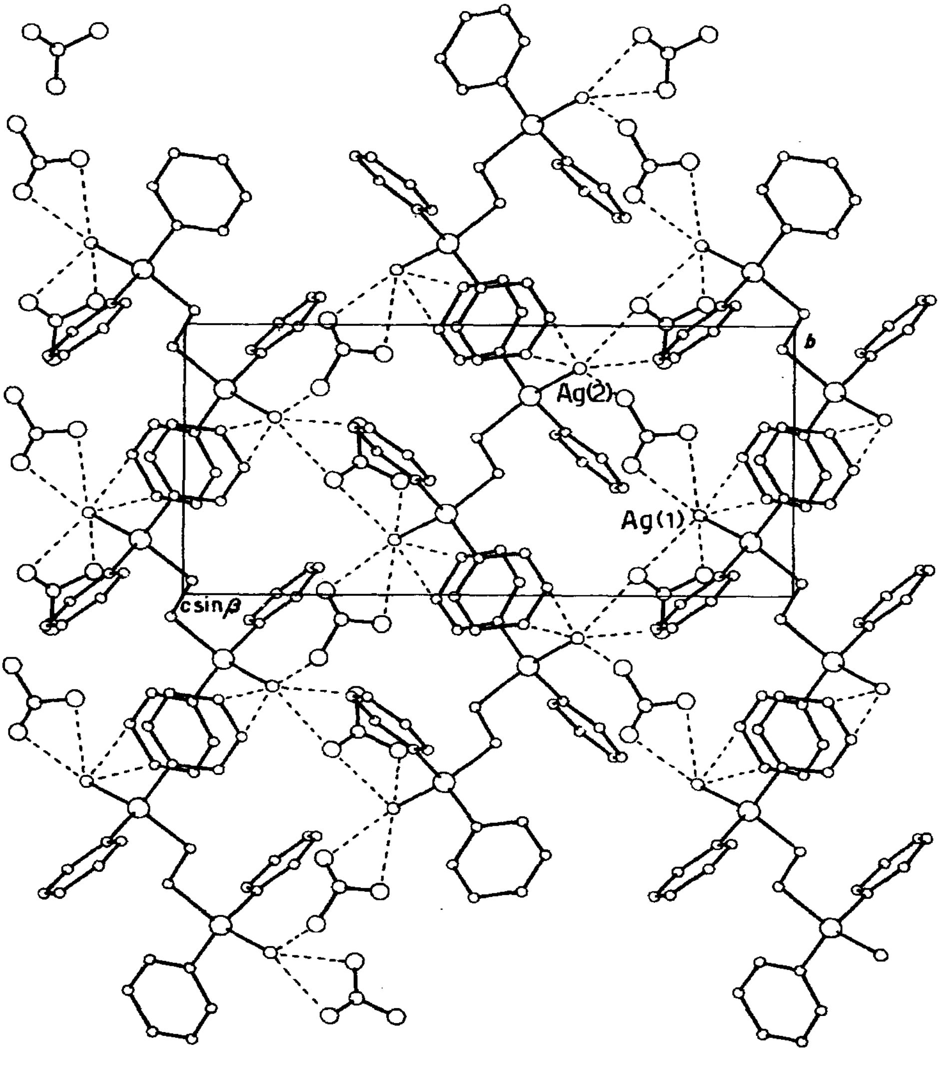

Fig. 3. Crystal structure of $(AgNO_3)_2(Ph_2AsCH_2CH_2AsPh_2)$ as seen along the a-axis.

2.71(3) Å, respectively. On the assumption that the bidentate nitrate groups as well as the phenyl rings each occupy only one coordination site, then the best description of the configuration about the two silver atoms is as a distorted tetrahedron.

The two independent Ag–As bond lengths average 2.473(6) Å, which agrees fairly well with the values of 2.471(2) and 2.488(6) Å estimated for $Ag(AsPh_3)NO_3$ [2] and for $C_{11}H_{15}AsAg_2(NO_3)_2$ [8], respectively. However, the difference between the two bonds in the present compound, 0.06 Å, is slightly, but statistically significant.

The tetrahedral coordination around the two As atoms is a little more regular than that in **1**, with the Ag–As–C angles always significantly larger than the C–As–C angles. The four independent As–C(sp^2) and the two independent As–C(sp^3) bond distances average 1.91(3) and 1.97(2) Å, respectively. The phenyl rings are planar within the limits of experimental error. Because of the low percentage of observed reflections and the high standard deviations, some of the C–C bond distances are poorly defined. In each Ph_2As moiety the aromatic rings are approximately perpendicular (81°, average) to each other and the As atom lies 0.05 Å (average) away from the best planes through the rings.

The two independent nitrate groups bond in a different manner. One, N(1)O(1)O(2)O(3), is coordinated to Ag(1) through O(1) and O(3) and bonds terminally to Ag(2) through O(2). The other, N(2)O(4)O(5)O(6), functions as a doubly-bidentate ligand bridging Ag(1) and Ag(2) through two asymmetric linkages; one of the oxygen atoms, O(4), is in a slightly asymmetrical bridging position. As already observed [2,8], the $Ag-O_{NO_3}$ bond lengths are spread over a rather large range of values (2.33(3)–2.73(3) Å). Bond angles subtended at the two Ag atoms by the bidentate nitrate groups (mean 48.9°) are fully comparable.

The infrared bands attributable to the diarsine ligand are scarcely influenced by the coordination effects, as can be seen from a comparison of the infrared absorptions of the complex with those of free dpae. In this case, also, the only bands which undergo (small) shifts are those involving the As–C stretching modes, which fall in the 1000 and 400 cm^{-1} regions.

It is difficult to relate the infrared bands due to the nitrate group to the ligand behaviour that it shows in the complex. The main vibrational bands involving the NO_3 group, which fall at 1445ms, 1380vs, br, 1280vs, 815w, 805w cm^{-1}, suggest the presence of a monodentate ($\Delta\nu = \nu_{as}(NO_3) - \nu_s(NO_3) = 165$ cm^{-1}) and an ionic nitrate group [9,10], whereas the actual structural situation is, as above mentioned, more complicated.

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