Chemical and Structural Aspects of Silver–Triphenylarsine Complexes and Silver–Tin Complex Salts†

Mario Nardelli,* Corrado Pelizzi, Giancarlo Pelizzi, and Pieralberto Tarasconi
Istituto di Chimica Generale ed Inorganica dell'Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Via M. D'Azeglio 85, 43100 Parma, Italy

Three compounds previously described as tin derivatives have been reinvestigated by *X*-ray diffraction and found to have the following formulae: $Ag(AsPh_3)(NO_3)$ (**1**) [monoclinic, space group $P2_1/c$, a = 10.405(5), b = 18.895(12), c = 9.138(6) Å, β = 98.35(8)°, Z = 4; R = 0.0450 for 2 036 reflections]; $Ag(AsPh_3)_2(NO_3)$ (**2**) [triclinic, space group $P\bar{1}$, a = 11.97(1), b = 12.02(1), c = 13.68(1) Å, α = 102.0(1), β = 113.3(1), γ = 104.0(1)°, Z = 2; R = 0.0468 for 4 409 reflections]; $Ag(AsPh_3)_3(NO_3)$ (**3**) [monoclinic, space group $P2_1/n$, a = 19.193(8), b = 14.003(7), c = 17.893(7) Å, β = 96.4(1)°, Z = 4; R = 0.0478 for 3 543 reflections]. In all these compounds the silver atom is co-ordinated, in an irregular fashion, by arsenic and oxygen atoms. In addition, two new silver–tin complex salts have been prepared and structurally characterized by *X*-ray diffraction: $[Ag(AsPh_3)_4][SnPh_2(NO_3)_3]$ (**4**) [triclinic, space group $P\bar{1}$, a = 22.57(2), b = 14.22(1), c = 14.07(1) Å, α = 90.9(1), β = 69.9(1), γ = 65.6(1)°, Z = 2; R = 0.0635 for 4 494 reflections] and $[Ag(AsPh_3)_4][SnPh_2(NO_3)_2Cl]$ (**5**) [triclinic, space group $P\bar{1}$, a = 22.68(2), b = 14.24(1), c = 14.24(1) Å, α = 90.66(6), β = 69.17(5), γ = 64.36(4)°, Z = 2; R = 0.0648 for 7 108 reflections]. These two compounds are isostructural and contain a tetrahedral $[Ag(AsPh_3)_4]^+$ cation and a bipyramidal anion in which the tin atom is co-ordinated apically by two phenyl groups; the equatorial sites are occupied by six oxygen atoms from three NO_3^- ions in (**4**), and by four oxygen atoms from two NO_3^- ions and a chlorine in (**5**).

From the reaction of $SnPh_2(NO_3)_2$ with $AsPh_3$ a series of compounds is obtained. Three of these have been characterized previously by *X*-ray diffraction and the formulae $Sn(SnPh_3)NO_3$, $Sn(SnPh_3)(AsPh_3)NO_3$, and $Sn(SnPh_3)_3NO_3$ were erroneously assigned to them.[1,2] In fact, development of this research has indicated that these were actually silver–arsine compounds, the metal deriving from $AgNO_3$ used as reagent together with $SnPh_2Cl_2$ in the preparation of $SnPh_2(NO_3)_2$. Evidence for this came from the *X*-ray analysis of a fourth compound obtained in the same preparation which was found to contain silver together with tin, its formula being $[Ag(AsPh_3)_4][SnPh_2(NO_3)_2Cl]$. The presence of silver was evidently due to incomplete purification of $SnPh_2(NO_3)_2$ from the excess of $AgNO_3$. This result prompted us to reinvestigate this reaction and to revise the nature of the previously characterized products to find explanations for some anomalies found: (i) exceptionally short Sn–C distances, (ii) Sn^{II}–Sn^{IV} bonds too short compared with Sn^{IV}–Sn^{IV} bonds, (iii) no lone-pair stereo effect exhibited by Sn^{II}. Therefore the structures of the first three compounds were redetermined assuming the presence of silver and the results showed that the formulae $Ag(AsPh_3)(NO_3)$ (**1**), $Ag(AsPh_3)_2(NO_3)$ (**2**), and $Ag(AsPh_3)_3(NO_3)$ (**3**) were the correct ones. To confirm these results, the same compounds were prepared directly from $AgNO_3$ and $AsPh_3$ and *X*-ray analyses carried out.

To reinvestigate the reaction with $SnPh_2(NO_3)_2$, this product was prepared using a stoicheiometric $AgNO_3:SnPh_2Cl_2$ molar ratio of 2:1 and then purified with complete elimination of silver. By reacting this product with $AsPh_3$ under the previously reported conditions, the oxidation of the arsine occurs, and the adduct $SnPh_2(NO_3)_2(AsPh_3O)$ is formed. The same compound is also obtained by changing the solvent and/or under an N_2 atmosphere. All its properties coincide with those of the product obtained directly from $SnPh_2(NO_3)_2$ and $AsPh_3O$, whose structure has been determined already.[3] To clarify further the mechanism of the reaction when $SnPh_2(NO_3)_2$ containing silver is used and with the aim of isolating new mixed silver–tin compounds, pure $SnPh_2(NO_3)_2$ and $AsPh_3$ were reacted with stoicheiometric amounts of AgCl or $AgNO_3$. In both cases a compound not containing chlorine and formed by silver complex cations and tin complex anions was isolated; from the *X*-ray analysis it was found to be isostructural with $[Ag(AsPh_3)_4][SnPh_2(NO_3)_2Cl]$ (**5**), having the formula $[Ag(AsPh_3)_4][SnPh_2(NO_3)_3]$ (**4**). Compound (**5**) can be obtained also by reacting $SnPh_2Cl_2$ with $Ag(AsPh_3)_3(NO_3)$, showing that the chlorine-containing complex is formed only by using $SnPh_2Cl_2$. All these compounds have been examined by *X*-ray crystal structure analysis.

Another compound prepared with $SnPh_2(NO_3)_2$ containing silver, (2-aminobenzothiazolato)nitratotin(II), has been described.[4] It is therefore well-grounded suspicion that also in this case a silver compound has been considered as a tin derivative. On the other hand, the replacement of silver with tin does not influence a great deal the C, H, and N analyses nor the *X*-ray diffraction results. Further research is in progress in our laboratory to define the correct nature of this compound.

The present paper deals with a reinvestigation of reactions in which $SnPh_2(NO_3)_2$, $AgNO_3$, and $AsPh_3$ are involved and with the crystal and molecular structures of compounds (**1**)—(**5**).

Experimental

Reactions.— (*a*) The reaction between $SnPh_2(NO_3)_2$ (which was subsequently found to be contamined by silver) and $AsPh_3$ was carried out at room temperature in acetone as described previously.[1,2] The first reaction product, not previously defined, is now identified as $[Ag(AsPh_3)_4][SnPh_2(NO_3)_2Cl]$ (**5**) by *X*-ray analysis. This compound, dissolved in acetone, by slow evaporation gave crystalline $Ag(AsPh_3)(NO_3)$ (**1**), while from the original parent solution two complexes, $Ag(AsPh_3)_2(NO_3)$ (**2**) and $Ag(AsPh_3)_3(NO_3)$ (**3**), were obtained by successive

† *Supplementary data available* (No. SUP 56080, 6 pp.): isotropic and anisotropic thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Crystallographic data and experimental details of the *X*-ray diffraction work

	$Ag(AsPh_3)(NO_3)$ (1)	$Ag(AsPh_3)_2(NO_3)$ (2)	$Ag(AsPh_3)_3(NO_3)$ (3)	$[Ag(AsPh_3)_4]$-$[SnPh_2(NO_3)_3]$ (4)	$[Ag(AsPh_3)_4]$-$[SnPh_2(NO_3)_2Cl]$ (5)
(*a*) Crystal data					
Formula	$C_{18}H_{15}AgAsNO_3$	$C_{36}H_{30}AgAs_2NO_3$	$C_{54}H_{45}AgAs_3NO_3$	$C_{84}H_{70}AgAs_4N_3O_9Sn$	$C_{84}H_{70}AgAs_4ClN_2O_6Sn$
M	476.11	782.35	1 088.59	1 791.74	1 765.18
Space group	$P2_1/c$ (monoclinic)	$P\bar{1}$ (triclinic)	$P2_1/n$ (monoclinic)	$P\bar{1}$ (triclinic)	$P\bar{1}$ (triclinic)
a/Å	10.405(5)	11.97(1)	19.193(8)	22.57(2)	22.68(2)
b/Å	18.895(12)	12.02(1)	14.003(7)	14.22(1)	14.24(1)
c/Å	9.138(6)	13.68(1)	17.893(7)	14.07(1)	14.24(1)
α/°	90	102.0(1)	90	90.9(1)	90.66(6)
β/°	98.35(8)	113.3(1)	96.4(1)	69.9(1)	69.17(5)
γ/°	90	104.0(1)	90	65.6(1)	64.36(4)
U/Å^3	1 778(2)	1 649(3)	4 779(4)	3 796(7)	3 800(6)
Z	4	2	4	2	2
D_c/g cm^{-3}	1.779	1.575	1.513	1.568	1.543
Reflections for lattice parameters: number	16	18	15	18	21
Reflections for lattice parameters: θ range (°)	13.6—20.9	8.9—17.3	11.5—20.2	12.2—17.7	10.4—29.0
Radiation, λ/Å	Mo-K_α, 0.710 69	Mo-K_α, 0.710 69	Mo-K_α, 0.710 69	Mo-K_α, 0.710 69	Cu-K_α, 1.541 78
F(000)	936	780	2 184	1 792	1 764
μ/cm^{-1}	29.8	26.2	25.2	23.7	74.9
(*b*) Data collection					
2θ limits (°)	6.0—52.0	5.0—50.0	5.0—50.0	6.0—48.0	6.0—110.0
Total reflections measured	3 822	5 808	9 067	11 262	9 524
Total unique reflections	3 486	5 808	8 426	11 262	9 524
Reflections with $I \geqslant 2\sigma(I)$	2 036	4 409	3 543	4 494	7 108
(*c*) Refinement details					
No. of parameters varied	217	388	559	439	427
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.0450	0.0468	0.0478	0.0635	0.0648
$R' = \Sigma\sqrt{w}\lvert\Delta F\rvert/\Sigma\sqrt{w}\lvert F_o\rvert$	0.0492	0.0523	0.0511	0.0628	0.0724

Table 2. Fractional atomic co-ordinates ($\times 10^5$ for Ag and As, $\times 10^4$ for O, N, and C) for $Ag(AsPh_3)(NO_3)$ (**1**)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Ag	1 723(6)	17 511(4)	8 028(8)	C(7)	2 055(6)	21(4)	992(8)
As	20 680(7)	10 147(4)	4 600(8)	C(8)	2 360(7)	−521(4)	12(9)
O(1)	284(6)	2 391(3)	3 287(7)	C(9)	2 436(8)	−1 222(4)	545(13)
O(2)	−898(5)	2 191(3)	4 990(6)	C(10)	2 184(8)	−1 376(5)	1 957(12)
O(3)	−1 012(7)	1 492(4)	3 085(8)	C(11)	1 875(8)	−848(5)	2 894(10)
N	−553(6)	2 023(4)	3 777(8)	C(12)	1 787(7)	−151(4)	2 378(9)
C(1)	3 632(7)	1 321(4)	1 698(7)	C(13)	2 595(6)	999(3)	−1 489(7)
C(2)	4 675(8)	863(4)	2 161(8)	C(14)	3 874(7)	908(4)	−1 709(8)
C(3)	5 757(8)	1 094(4)	3 061(10)	C(15)	4 200(7)	920(4)	−3 120(9)
C(4)	5 819(9)	1 782(5)	3 596(12)	C(16)	3 237(9)	980(5)	−4 335(9)
C(5)	4 791(10)	2 245(5)	3 150(13)	C(17)	1 950(10)	1 068(5)	−4 111(10)
C(6)	3 717(8)	2 015(4)	2 222(11)	C(18)	1 651(8)	1 091(5)	−2 694(9)

filtrations and evaporations. The remaining residue of the original solution was found to be a mixture of organotin derivatives, such as $[SnPh_2(NO_3)]_2O$, $SnPh_2(OH)(NO_3)$, and $[SnPh_2(OH)]_2O$, originating from hydrolysis processes caused by air moisture.[5,6] These derivatives were mainly responsible for the analytical data giving the incorrect formulae reported previously.

(*b*) The three $Ag(AsPh_3)_n(NO_3)$ (n = 1—3) complexes were prepared again by reacting stoicheiometric amounts of triphenylarsine in acetone and silver nitrate in acetonitrile with stirring at room temperature. By slow evaporation of the three solutions, colourless crystals were isolated for each compound. Analytical, spectroscopic, and crystallographic data are identical with those of (**1**), (**2**) and (**3**), so confirming the assigned formulae. All the compounds slowly blacken in light after long exposure. Compound (**1**) (Found: C, 45.05; H, 2.95; Ag, 23.25; N, 2.9. $C_{18}H_{15}AgAsNO_3$ requires C, 45.4; H, 3.20; Ag, 22.65; N, 2.95%). Compound (**2**) (Found: C, 55.1; H, 3.95; Ag, 14.2; N, 1.85. $C_{36}H_{30}AgAs_2NO_3$ requires C, 55.25; H, 3.85; Ag, 13.8; N, 1.80%). Compound (**3**) (Found: C, 59.7; H, 4.25; Ag, 8.45; N, 1.15. $C_{54}H_{45}AgAs_3NO_3$ requires C, 59.6; H, 4.15; Ag, 9.90; N, 1.30%).

(*c*) $SnPh_2(NO_3)_2$ was prepared again following the previously described procedure,[7] by using rigorously checked stoicheiometric amounts of the reagents. Silver salts were precipitated by successive additions of small portions of chloroform to the acetonitrile solution and removed by filtration. At the end, the volume of the solution was reduced and a white crystalline product was obtained. The analysis carried out by atomic absorption spectroscopy confirmed the absence of silver in this compound.

(*d*) To verify the formation of different tin adducts, $SnPh_2(NO_3)_2$ [prepared as described in (*c*)] and $AsPh_3$ were reacted in acetone solution in 1:1, 1:2, and 1:3 molar ratios. In all cases

Table 3. Fractional atomic co-ordinates ($\times 10^5$ for Ag and As, $\times 10^4$ for O, N, and C) for $Ag(AsPh_3)_2(NO_3)$ (**2**)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Ag	7 634(4)	18(4)	16 935(4)	C(16)	5 627(9)	1 835(9)	6 496(7)
As(1)	26 019(5)	19 951(5)	30 708(5)	C(17)	6 033(7)	2 698(8)	6 062(7)
As(2)	−7 867(5)	−16 741(5)	18 823(5)	C(18)	5 158(6)	2 755(7)	5 032(6)
O(1)	813(4)	−712(4)	−65(4)	C(19)	−2 475(5)	−1 591(6)	1 578(5)
O(2)	2 249(5)	−1 126(5)	1 197(4)	C(20)	−2 651(7)	−513(7)	1 498(5)
O(3)	1 951(5)	−1 673(5)	−527(5)	C(21)	−3 846(10)	−427(10)	1 275(7)
N	1 680(5)	−1 182(4)	193(5)	C(22)	−4 854(9)	−1 411(13)	1 155(7)
C(1)	1 995(6)	3 228(5)	3 600(6)	C(23)	−4 678(8)	−2 462(11)	1 225(8)
C(2)	2 674(8)	4 079(7)	4 688(7)	C(24)	−3 510(6)	−2 580(8)	1 432(7)
C(3)	2 172(9)	4 930(8)	5 023(9)	C(25)	−114(5)	−1 778(5)	3 397(5)
C(4)	975(10)	4 877(8)	4 252(11)	C(26)	1 090(6)	−1 901(6)	3 823(6)
C(5)	297(10)	4 033(11)	3 194(10)	C(27)	1 686(8)	−1 909(7)	4 922(7)
C(6)	784(8)	3 180(8)	2 874(7)	C(28)	1 077(9)	−1 789(7)	5 574(7)
C(7)	3 723(6)	2 843(5)	2 549(5)	C(29)	−122(10)	−1 641(9)	5 170(7)
C(8)	4 056(7)	4 096(6)	2 736(6)	C(30)	−733(8)	−1 660(8)	4 033(6)
C(9)	4 860(8)	4 652(8)	2 350(8)	C(31)	−1 201(5)	−3 324(5)	954(5)
C(10)	5 279(11)	3 973(10)	1 745(9)	C(32)	−1 467(7)	−4 309(5)	1 286(6)
C(11)	4 958(12)	2 698(10)	1 548(9)	C(33)	−1 771(7)	−5 480(6)	558(7)
C(12)	4 176(9)	2 160(7)	1 969(7)	C(34)	−1 788(6)	−5 636(6)	−451(7)
C(13)	3 865(6)	1 952(5)	4 477(5)	C(35)	−1 503(6)	−4 639(7)	−802(6)
C(14)	3 463(8)	1 107(8)	4 903(6)	C(36)	−1 193(6)	−3 477(5)	−82(5)
C(15)	4 324(11)	1 031(10)	5 902(8)				

Table 4. Fractional atomic co-ordinates ($\times 10^5$ for Ag, $\times 10^4$ for As, O, N, and C) for $Ag(AsPh_3)_3(NO_3)$ (**3**)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Ag	192(4)	19 170(6)	22 773(5)	C(24)	−1 569(6)	−461(9)	3 411(7)
As(1)	1 184(1)	2 015(1)	1 657(1)	C(25)	−394(5)	−901(7)	1 898(6)
As(2)	−418(1)	202(1)	2 572(1)	C(26)	193(5)	−997(8)	1 497(6)
As(3)	24(1)	3 167(1)	3 410(1)	C(27)	222(7)	−1 749(9)	986(6)
O(1)	−658(9)	2 108(11)	939(9)	C(28)	−315(7)	−2 427(9)	895(7)
O(2)	−931(7)	3 017(11)	1 658(6)	C(29)	−905(7)	−2 329(9)	1 307(7)
O(3)	−1 495(6)	2 997(8)	567(6)	C(30)	−965(7)	−1 552(9)	1 803(7)
N	−1 056(5)	2 735(8)	1 047(7)	C(31)	153(5)	−256(8)	3 463(6)
C(1)	1 444(5)	976(8)	1 013(6)	C(32)	343(8)	−1 180(11)	3 548(8)
C(2)	2 080(6)	454(9)	1 165(7)	C(33)	788(9)	−1 463(11)	4 207(9)
C(3)	2 207(7)	−305(9)	700(8)	C(34)	1 031(7)	−798(12)	4 695(8)
C(4)	1 728(7)	−567(9)	98(7)	C(35)	832(10)	137(12)	4 594(8)
C(5)	1 105(7)	−57(9)	−54(7)	C(36)	396(9)	407(9)	3 986(6)
C(6)	961(7)	736(9)	433(7)	C(37)	−907(5)	3 406(8)	3 742(6)
C(7)	1 986(6)	2 026(9)	2 414(6)	C(38)	−1 057(6)	4 252(8)	4 079(7)
C(8)	2 449(7)	2 797(10)	2 498(7)	C(39)	−1 730(6)	4 393(10)	4 295(7)
C(9)	3 008(7)	2 762(12)	3 083(8)	C(40)	−2 226(7)	3 641(11)	4 199(8)
C(10)	3 062(8)	1 950(14)	3 565(8)	C(41)	−2 069(7)	2 809(11)	3 854(8)
C(11)	2 586(10)	1 230(13)	3 487(9)	C(42)	−1 393(6)	2 674(9)	3 615(7)
C(12)	2 021(7)	1 239(10)	2 901(7)	C(43)	272(6)	4 474(7)	3 163(7)
C(13)	1 311(6)	3 116(8)	1 026(6)	C(44)	797(8)	4 991(10)	3 568(10)
C(14)	1 862(7)	3 156(9)	559(6)	C(45)	920(8)	5 981(13)	3 281(15)
C(15)	1 897(7)	3 988(11)	97(7)	C(46)	509(13)	6 242(15)	2 602(14)
C(16)	1 410(9)	4 722(10)	104(8)	C(47)	−1(15)	5 767(15)	2 282(11)
C(17)	876(8)	4 658(10)	568(9)	C(48)	−138(9)	4 845(10)	2 500(8)
C(18)	822(7)	3 853(10)	1 023(7)	C(49)	611(6)	2 996(7)	4 351(6)
C(19)	−1 385(5)	131(8)	2 828(6)	C(50)	1 310(6)	2 726(8)	4 317(7)
C(20)	−1 884(7)	626(10)	2 388(7)	C(51)	1 760(7)	2 629(9)	4 987(7)
C(21)	−2 597(7)	571(11)	2 518(8)	C(52)	1 516(8)	2 810(9)	5 663(7)
C(22)	−2 787(7)	−19(11)	3 080(8)	C(53)	839(9)	3 106(11)	5 720(8)
C(23)	−2 293(8)	−551(10)	3 524(8)	C(54)	363(7)	3 196(10)	5 044(7)

the same white crystalline product of formula $SnPh_2(NO_3)_2$-$(AsPh_3O)$ was obtained, together with the excess of the arsenic reagent. The same product had been obtained previously from the reaction of $SnPh_2(NO_3)_2$ and $AsPh_3O$ in equimolar amounts.[3] Attempts to isolate nitratotin adducts containing unoxidized triphenylarsine have been carried out also under an N_2 atmosphere in dry acetonitrile; in this case $SnPh_2(NO_3)_2$-$(AsPh_3O)$ was obtained also.

(*e*) To verify the formation of silver–tin-containing adducts also in the absence of triphenylarsine, very finely powdered AgCl (or $AgNO_3$) was added to $SnPh_2(NO_3)_2$ dissolved in acetonitrile and the resulting suspension was treated as in (*a*). In both cases no reaction occurred.

(*f*) Finely powdered AgCl or $AgNO_3$ (0.5 mmol) was added to an acetone solution of $SnPh_2(NO_3)_2$ (0.5 mmol) containing $AsPh_3$ (2.0 mmol). The mixture was warmed to 50—60 °C and stirred for 1 h and the resulting solution was allowed to stand overnight. After some days, in both cases a colourless crystalline

Table 5. Fractional atomic co-ordinates (× 10^4) for $[Ag(AsPh_3)_4][SnPh_2(NO_3)_3]$ (4)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Sn	2 164(1)	5 710(1)	8 853(1)	C(34)	31(9)	3 831(14)	7 818(14)
Ag	2 520(1)	409(1)	3 737(1)	C(35)	334(9)	4 400(14)	7 215(14)
As(1)	2 161(1)	−1 049(1)	4 561(1)	C(36)	800(9)	3 958(13)	6 173(13)
As(2)	1 446(1)	2 367(1)	4 310(1)	C(37)	3 379(9)	653(13)	917(13)
As(3)	3 017(1)	−241(1)	1 707(1)	C(38)	3 053(10)	1 708(15)	1 355(14)
As(4)	3 505(1)	400(1)	4 351(1)	C(39)	3 283(10)	2 413(15)	795(15)
O(1)	2 062(8)	5 375(11)	7 226(10)	C(40)	3 825(12)	2 059(18)	−149(17)
O(2)	2 958(7)	4 284(11)	7 495(11)	C(41)	4 144(12)	977(18)	−591(17)
O(3)	2 832(9)	4 035(14)	6 066(15)	C(42)	3 943(10)	229(15)	−20(15)
O(4)	3 141(8)	4 666(12)	9 320(12)	C(43)	2 336(9)	−249(15)	1 112(14)
O(5)	2 295(7)	6 073(10)	10 435(10)	C(44)	2 089(11)	−972(16)	1 386(15)
O(6)	3 225(10)	5 241(15)	10 709(16)	C(45)	1 586(11)	−1 007(17)	1 031(17)
O(7)	1 142(8)	6 897(12)	8 718(12)	C(46)	1 361(11)	−252(18)	447(17)
O(8)	1 074(9)	7 283(12)	10 202(13)	C(47)	1 594(12)	480(18)	161(17)
O(9)	173(10)	8 046(14)	9 826(13)	C(48)	2 147(10)	476(15)	488(15)
N(1)	2 631(11)	4 555(16)	6 962(15)	C(49)	3 805(9)	−1 631(13)	1 090(13)
N(2)	2 915(11)	5 293(16)	10 101(16)	C(50)	3 850(11)	−2 220(17)	212(17)
N(3)	771(11)	7 448(14)	9 628(15)	C(51)	4 444(13)	−3 255(19)	−161(18)
C(1)	1 657(8)	−747(13)	6 055(13)	C(52)	4 947(12)	−3 608(17)	268(18)
C(2)	1 241(9)	−1 244(13)	6 518(13)	C(53)	4 875(11)	−3 052(18)	1 130(17)
C(3)	827(9)	−919(14)	7 600(14)	C(54)	4 294(10)	−2 016(15)	1 550(15)
C(4)	828(11)	−108(17)	8 156(16)	C(55)	3 240(9)	823(14)	5 825(13)
C(5)	1 267(13)	348(18)	7 695(19)	C(56)	2 602(11)	1 769(16)	6 320(16)
C(6)	1 707(10)	−13(15)	6 629(16)	C(57)	2 388(12)	2 120(18)	7 382(18)
C(7)	1 454(8)	−1 087(12)	4 113(12)	C(58)	2 775(12)	1 549(18)	7 893(17)
C(8)	1 407(9)	−1 984(13)	3 873(13)	C(59)	3 424(12)	615(17)	7 428(17)
C(9)	873(10)	−1 931(14)	3 513(14)	C(60)	3 662(10)	234(15)	6 345(15)
C(10)	405(9)	−967(14)	3 419(13)	C(61)	4 274(9)	−1 001(13)	4 074(12)
C(11)	460(9)	−61(13)	3 679(13)	C(62)	4 088(10)	−1 789(15)	4 429(14)
C(12)	980(9)	−101(13)	4 032(13)	C(63)	4 626(12)	−2 845(17)	4 264(17)
C(13)	2 812(8)	−2 555(12)	4 275(13)	C(64)	5 321(12)	−3 042(17)	3 702(17)
C(14)	2 901(10)	−3 078(15)	5 063(14)	C(65)	5 520(10)	−2 273(16)	3 340(15)
C(15)	3 400(11)	−4 179(17)	4 783(16)	C(66)	4 966(10)	−1 203(14)	3 508(14)
C(16)	3 757(11)	−4 651(17)	3 782(18)	C(67)	4 023(9)	1 177(13)	3 726(13)
C(17)	3 685(11)	−4 124(17)	2 976(16)	C(68)	4 167(10)	1 237(15)	2 691(15)
C(18)	3 182(10)	−3 020(16)	3 261(15)	C(69)	4 532(10)	1 790(15)	2 194(15)
C(19)	1 742(8)	3 430(12)	3 802(12)	C(70)	4 749(10)	2 306(14)	2 739(15)
C(20)	1 385(8)	4 179(13)	3 311(12)	C(71)	4 632(11)	2 249(16)	3 759(17)
C(21)	1 613(10)	4 945(14)	2 929(14)	C(72)	4 232(10)	1 713(15)	4 307(14)
C(22)	2 181(11)	4 948(15)	3 070(15)	C(73)	2 730(10)	6 546(15)	8 216(14)
C(23)	2 533(10)	4 219(15)	3 580(15)	C(74)	2 400(12)	7 606(19)	8 288(18)
C(24)	2 291(10)	3 447(14)	3 972(14)	C(75)	2 831(15)	8 139(20)	7 857(20)
C(25)	670(9)	2 658(13)	3 863(13)	C(76)	3 526(16)	7 639(24)	7 338(21)
C(26)	−47(9)	3 338(13)	4 566(13)	C(77)	3 868(16)	6 551(26)	7 286(21)
C(27)	−584(10)	3 509(14)	4 200(14)	C(78)	3 477(14)	5 970(19)	7 724(19)
C(28)	−428(9)	3 052(13)	3 205(14)	C(79)	1 649(8)	4 779(12)	9 497(12)
C(29)	279(10)	2 381(14)	2 544(14)	C(80)	1 169(9)	4 727(13)	9 152(13)
C(30)	812(9)	2 194(14)	2 891(13)	C(81)	855(11)	4 051(16)	9 536(16)
C(31)	904(8)	2 961(12)	5 780(11)	C(82)	1 018(11)	3 472(16)	10 274(16)
C(32)	647(9)	2 347(13)	6 370(13)	C(83)	1 501(11)	3 578(16)	10 606(16)
C(33)	164(9)	2 830(14)	7 414(14)	C(84)	1 841(10)	4 203(15)	10 229(15)

product of formula $[Ag(AsPh_3)_4][SnPh_2(NO_3)_3]$ (4) was formed (Found: C, 55.85; H, 3.90; Ag, 5.10; N, 2.35; Sn, 6.80. $C_{84}H_{70}AgAs_4N_3O_9Sn$ requires C, 56.3; H, 3.95; Ag, 6.00; N, 2.35; Sn, 6.65%).

(*g*) $SnPh_2Cl_2$ (0.5 mmol) dissolved in acetone was added to a solution, in the same solvent, of $Ag(AsPh_3)_3(NO_3)$ in slight excess (0.6 mmol), and the mixture was vigorously stirred at room temperature for 2 h. AgCl immediately formed and was then removed by filtration. The volume of the remaining solution was reduced under vacuum and dry chloroform (20 cm^3) was added to the residual solution. The suspension was filtered again and the resulting filtrate was concentrated to dryness under vacuum. Recrystallization from acetone of the crude residue gave, as main reaction product, $[Ag(AsPh_3)_4][SnPh_2(NO_3)_2Cl]$ (5) (Found: C, 56.4; H, 4.00; Ag, 6.35; N, 2.35; Sn, 6.60. $C_{84}H_{70}AgAs_4ClN_2O_6Sn$ requires C, 57.15; H, 4.00; Ag, 6.10; N, 1.60; Sn, 6.70%).

Collection and Reduction of X-*Ray Data*.—For all the five compounds, crystal symmetry and preliminary crystal data were obtained from oscillation and Weissenberg photographs taken with Cu-K_α radiation and precise unit-cell dimensions were calculated from least-squares fits to the diffractometer-measured θ angles of 15—20 reflections, well distributed in reciprocal space. In each case, the intensity data were collected at 22 °C on a Siemens automatic diffractometer controlled by a G.A. 220 computer, using the moving-counter moving-crystal scan technique, with Mo-K_α radiation [except for compound

Table 6. Fractional atomic co-ordinates ($\times 10^5$ for Sn and Ag, $\times 10^4$ for As, Cl, O, N, and C) for $[Ag(AsPh_3)_4][SnPh_2(NO_3)_2Cl]$ (**5**)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Sn	20 041(5)	58 952(7)	90 455(6)	C(36)	808(7)	3 931(10)	6 215(9)
Ag	25 476(4)	3 500(6)	37 601(6)	C(37)	3 402(6)	593(8)	961(8)
As(1)	2 156(1)	−1 053(1)	4 614(1)	C(38)	3 077(7)	1 653(10)	1 399(9)
As(2)	1 465(1)	2 350(1)	4 330(1)	C(39)	3 298(7)	2 342(11)	864(10)
As(3)	3 060(1)	−309(1)	1 726(1)	C(40)	3 821(8)	2 008(12)	−85(12)
As(4)	3 550(1)	295(1)	4 345(1)	C(41)	4 156(9)	939(14)	−585(13)
Cl	859(3)	7 511(4)	9 736(4)	C(42)	3 948(8)	194(11)	−15(11)
O(1)	1 790(6)	5 831(10)	7 620(9)	C(43)	2 430(6)	−348(8)	1 101(8)
O(2)	2 761(6)	4 450(9)	7 321(9)	C(44)	2 145(7)	−1 038(10)	1 393(10)
O(3)	2 257(6)	4 741(9)	6 235(9)	C(45)	1 662(8)	−1 079(12)	994(11)
O(4)	3 017(6)	4 897(9)	9 768(9)	C(46)	1 441(9)	−368(13)	363(13)
O(5)	2 077(5)	6 259(8)	10 574(7)	C(47)	1 721(8)	312(13)	75(12)
O(6)	2 960(6)	5 729(9)	11 030(9)	C(48)	2 239(7)	341(10)	455(10)
N(1)	2 296(7)	4 988(10)	7 057(10)	C(49)	3 880(6)	−1 725(9)	1 116(8)
N(2)	2 685(7)	5 591(11)	10 426(11)	C(50)	3 977(8)	−2 318(11)	221(11)
C(1)	1 636(6)	−715(9)	6 110(9)	C(51)	4 588(9)	−3 334(13)	−151(12)
C(2)	1 217(7)	−1 202(10)	6 585(10)	C(52)	5 040(9)	−3 667(13)	291(13)
C(3)	773(7)	−843(11)	7 666(11)	C(53)	4 956(9)	−3 109(13)	1 165(12)
C(4)	796(8)	−56(12)	8 212(12)	C(54)	4 369(8)	−2 107(11)	1 567(11)
C(5)	1 228(9)	419(13)	7 759(13)	C(55)	3 269(6)	721(8)	5 789(8)
C(6)	1 667(8)	53(11)	6 683(11)	C(56)	2 629(7)	1 715(11)	6 294(10)
C(7)	1 453(5)	−1 087(8)	4 161(8)	C(57)	2 420(8)	2 075(12)	7 350(12)
C(8)	1 430(6)	−2 028(10)	3 936(9)	C(58)	2 844(8)	1 472(13)	7 849(12)
C(9)	907(7)	−1 966(10)	3 573(9)	C(59)	3 433(8)	506(13)	7 413(12)
C(10)	450(7)	−1 015(10)	3 426(9)	C(60)	3 660(7)	148(10)	6 322(10)
C(11)	472(6)	−59(10)	3 660(9)	C(61)	4 354(6)	−1 097(8)	4 053(8)
C(12)	981(6)	−135(9)	4 035(8)	C(62)	4 165(7)	−1 912(10)	4 419(10)
C(13)	2 820(6)	−2 558(9)	4 350(9)	C(63)	4 763(8)	−2 986(11)	4 222(11)
C(14)	2 904(8)	−3 084(12)	5 160(11)	C(64)	5 457(8)	−3 152(12)	3 680(11)
C(15)	3 415(9)	−4 174(14)	4 890(13)	C(65)	5 623(7)	−2 363(11)	3 346(10)
C(16)	3 803(9)	−4 693(13)	3 863(13)	C(66)	5 056(6)	−1 304(9)	3 526(9)
C(17)	3 762(9)	−4 208(14)	3 066(13)	C(67)	4 026(5)	1 119(8)	3 742(8)
C(18)	3 218(8)	−3 058(12)	3 335(11)	C(68)	4 166(7)	1 177(10)	2 711(9)
C(19)	1 747(5)	3 429(8)	3 833(8)	C(69)	4 502(7)	1 773(11)	2 208(10)
C(20)	1 399(6)	4 166(9)	3 303(8)	C(70)	4 724(7)	2 280(10)	2 780(10)
C(21)	1 656(7)	4 900(10)	2 952(10)	C(71)	4 593(7)	2 217(11)	3 786(11)
C(22)	2 208(7)	4 908(10)	3 102(10)	C(72)	4 224(6)	1 652(9)	4 300(8)
C(23)	2 528(7)	4 202(10)	3 650(10)	C(73)	2 719(9)	6 507(13)	8 288(12)
C(24)	2 318(6)	3 427(9)	3 999(9)	C(74)	2 451(10)	7 536(15)	8 169(14)
C(25)	693(5)	2 638(8)	3 884(8)	C(75)	2 920(13)	7 959(19)	7 678(18)
C(26)	−15(6)	3 307(9)	4 517(9)	C(76)	3 629(12)	7 362(17)	7 327(16)
C(27)	−572(6)	3 496(9)	4 146(9)	C(77)	3 946(12)	6 298(18)	7 390(17)
C(28)	−369(7)	2 999(10)	3 169(10)	C(78)	3 467(11)	5 874(16)	7 962(15)
C(29)	346(7)	2 300(10)	2 548(9)	C(79)	1 635(8)	4 759(11)	9 538(11)
C(30)	868(6)	2 135(9)	2 897(9)	C(80)	1 153(9)	4 705(13)	9 227(12)
C(31)	908(5)	2 966(8)	5 786(8)	C(81)	842(9)	4 019(14)	9 601(13)
C(32)	562(6)	2 444(9)	6 388(9)	C(82)	1 070(10)	3 396(15)	10 254(14)
C(33)	128(7)	2 886(10)	7 408(10)	C(83)	1 563(10)	3 442(15)	10 578(14)
C(34)	4(7)	3 864(10)	7 848(9)	C(84)	1 866(9)	4 158(14)	10 194(13)
C(35)	335(7)	4 394(11)	7 267(10)				

(**5**) for which Cu-K_α radiation was employed]. A complete set of the relevant crystallographic parameters and a summary of the data collection and structure refinement details for all compounds is given in Table 1. Metal-foil attenuators were automatically inserted if the diffracted beam exceeded an intensity of *ca.* 9 000 counts per second. A reference reflection was monitored for each crystal during the course of the experiment as a check on electronic and crystal stability, but no significant changes in intensity were observed. The data were corrected for Lorentz and polarization factors, but not for absorption due to difficulties in defining the crystal shape.

Solution and Refinement of the Structures.—Solution of the structures of (**1**)—(**3**) was carried out by conventional Patterson and Fourier techniques, while the structure of (**5**) was solved by a combination of direct methods and the heavy-atom technique. For compound (**4**) the atomic parameters of (**5**) were used as starting parameters, the two compounds being isostructural, and a subsequent ΔF map revealed the sites of the third NO_3^- ion. All the five structures were refined using full-matrix least-squares calculations, in each case minimizing the function $\Sigma w(|F_o| - |F_c|)^2$. Towards the end of refinement the weighting scheme was changed from unit to $w = k[\sigma^2(F_o) + |g|(F_o)^2]^{-1}$ and this gave appreciably lower standard deviations. All the atoms of (**1**)—(**3**) were refined anisotropically, while for (**4**) and (**5**) only the heaviest atoms (Ag, Sn, As) were given anisotropic thermal parameters, the remaining atoms being refined isotropically. In all refinements no constraint to the phenyl rings was applied. For all compounds, except (**1**), during the final stages of the refinement the atomic parameters had to be divided into two or three blocks, due to limitations on computer memory. In no case were attempts made to locate the

Table 7. Selected bond distances (Å) and angles (°) in the $Ag(AsPh_3)_n(NO_3)$ derivatives (**1**)—(**3**)

(**1**)		(**2**)		(**3**)	
(*a*) Silver environment					
Ag–As	2.471(2)	Ag–As(1)	2.535(5)	Ag–As(1)	2.608(3)
		Ag–As(2)	2.521(3)	Ag–As(2)	2.617(2)
				Ag–As(3)	2.678(2)
Ag–O(1)	2.560(6)	Ag–O(1)	2.409(6)	Ag–O(1)	2.607(16)
Ag–O(3)	2.618(8)	Ag–O(2)	2.684(7)	Ag–O(2)	2.544(14)
Ag–O(1^{i})	2.829(6)	Ag–O(1^{ii})	2.737(6)		
Ag–O(2^{i})	2.355(6)				
Ag–C(9^{ii})	2.985(8)				
		As(1)–Ag–As(2)	134.2(1)	As(1)–Ag–As(2)	116.3(1)
				As(1)–Ag–As(3)	110.9(1)
				As(2)–Ag–As(3)	114.9(1)
As–Ag–O(1)	116.4(2)	As(1)–Ag–O(1)	113.7(3)	As(1)–Ag–O(1)	88.1(4)
As–Ag–O(3)	118.2(2)	As(1)–Ag–O(2)	96.6(3)	As(1)–Ag–O(2)	112.9(3)
As–Ag–O(1^{i})	95.3(3)	As(1)–Ag–O(1^{ii})	102.9(2)	As(2)–Ag–O(1)	98.1(4)
As–Ag–O(2^{i})	141.9(2)	As(2)–Ag–O(1)	110.1(3)	As(2)–Ag–O(2)	114.4.(3)
		As(2)–Ag–O(2)	101.7(3)	As(3)–Ag–O(1)	126.0(4)
		As(2)–Ag–O(1^{ii})	104.7(3)	As(3)–Ag–O(2)	82.9(3)
O(1)–Ag–O(3)	49.3(2)	O(1)–Ag–O(2)	49.5(2)	O(1)–Ag–O(2)	43.8(4)
O(1)–Ag–O(1^{i})	116.6(4)	O(1)–Ag–O(1^{ii})	68.7(2)		
O(1)–Ag–O(2^{i})	80.6(2)	O(2)–Ag–O(1^{ii})	117.9(2)		
O(3)–Ag–O(1^{i})	146.5(4)				
O(3)–Ag–O(2^{i})	98.9(2)				
O(1^{i})–Ag–O(2^{i})	48.0(2)				
(*b*) Arsenic environment					
As–C(1)	1.931(7)	As(1)–C(1)	1.934(8)	As(1)–C(1)	1.955(11)
As–C(7)	1.941(8)	As(1)–C(7)	1.936(8)	As(1)–C(7)	1.934(11)
As–C(13)	1.938(7)	As(1)–C(13)	1.941(7)	As(1)–C(13)	1.942(11)
		As(2)–C(19)	1.928(7)	As(2)–C(19)	1.963(10)
		As(2)–C(25)	1.948(7)	As(2)–C(25)	1.963(10)
		As(2)–C(31)	1.942(6)	As(2)–C(31)	1.940(10)
				As(3)–C(37)	1.973(10)
				As(3)–C(43)	1.954(10)
				As(3)–C(49)	1.934(11)
Ag–As–C(1)	112.2(2)	Ag–As(1)–C(1)	113.0(4)	Ag–As(1)–C(1)	119.9(3)
Ag–As–C(7)	118.6(2)	Ag–As(1)–C(7)	118.0(2)	Ag–As(1)–C(7)	110.8(3)
Ag–As–C(13)	117.6(2)	Ag–As(1)–C(13)	117.1(3)	Ag–As(1)–C(13)	117.3(4)
		Ag–As(2)–C(19)	117.2(4)	Ag–As(2)–C(19)	115.2(3)
		Ag–As(2)–C(25)	113.3(3)	Ag–As(2)–C(25)	124.6(3)
		Ag–As(2)–C(31)	116.0(3)	Ag–As(2)–C(31)	107.7(3)
				Ag–As(3)–C(37)	114.3(3)
				Ag–As(3)–C(43)	114.9(4)
				Ag–As(3)–C(49)	122.1(3)
C(1)–As–C(7)	100.3(3)	C(1)–As(1)–C(7)	102.4(4)	C(1)–As(1)–C(7)	100.6(5)
C(1)–As–C(13)	102.5(3)	C(1)–As(1)–C(13)	102.3(4)	C(1)–As(1)–C(13)	101.0(5)
C(7)–As–C(13)	103.2(3)	C(7)–As(1)–C(13)	101.7(4)	C(7)–As(1)–C(13)	105.0(5)
		C(19)–As(2)–C(25)	103.0(4)	C(19)–As(2)–C(25)	101.0(5)
		C(19)–As(2)–C(31)	103.4(4)	C(19)–As(2)–C(31)	104.7(5)
		C(25)–As(2)–C(31)	101.9(4)	C(25)–As(2)–C(31)	101.2(5)
				C(37)–As(3)–C(43)	99.3(5)
				C(37)–As(3)–C(49)	102.6(5)
				C(43)–As(3)–C(49)	100.4(5)

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

hydrogen atoms. For each structure the final difference map was essentially devoid of any significant features. A complete structure analysis was carried out also on the complex which was obtained by reacting $SnPh_2Cl_2$ with $Ag(AsPh_3)_3(NO_3)$ as described in section (*g*) of the Experimental section. The results perfectly agree with those obtained for compound (**5**) showing the presence of chlorine; no further *X*-ray work was carried out on it. The scattering factors used were for neutral atoms and allowance was made for anomalous dispersion.[8] The final atomic co-ordinates with estimated standard deviations are listed in Tables 2—6. The computations were performed using the SHELX 76 program system[9] on the Cyber 76 Computer of C.I.N.E.C.A., with financial support from University of Parma. Selected bond distances and angles are listed in Table 7 for (**1**)—(**3**) and in Table 8 for (**4**) and (**5**). Figures 1—3 are perspective views of the three $Ag(AsPh_3)_n(NO_3)$ structures, (**1**)—(**3**). The cation in (**4**) and (**5**) is illustrated in Figure 4, while Figures 5 and 6 are drawings of the anion in (**4**) and (**5**) respectively. Additional programs used were PARST[10] and PLUTO.[11]

Results and Discussion

The results of this structural study have revealed a number of significant features. (*i*) We believe this is the first reported

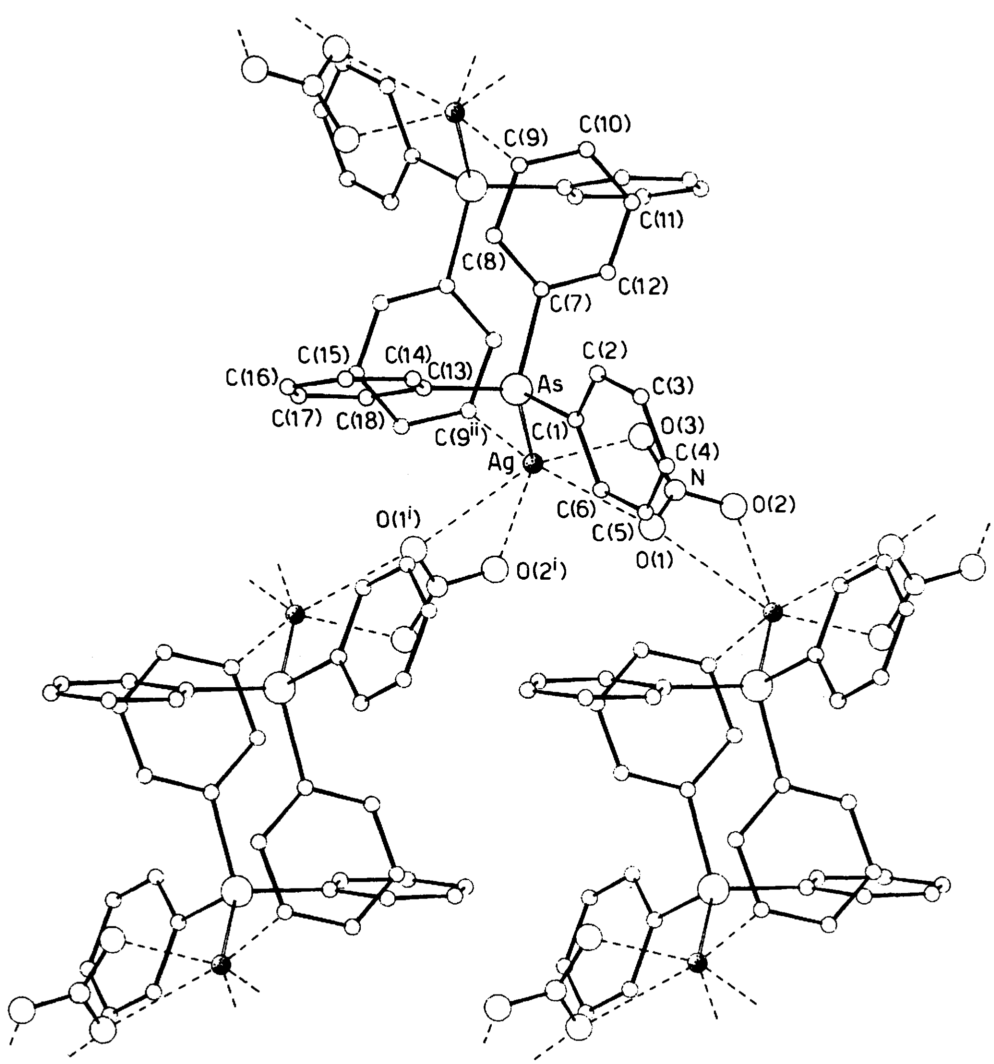

Figure 1. Molecular structure of $Ag(AsPh_3)(NO_3)$ (1)

case of a complex, characterized by *X*-ray crystal structure analysis, where a metal atom is bonded to four $AsPh_3$ groups. (*ii*) To our knowledge, the coexistence, in both (**4**) and (**5**), of silver and tin has not been found previously. (*iii*) Ag–As bonds are present in all five compounds. Only two *X*-ray structure determinations of compounds containing such a bond have been reported in the literature: {[bis(*o*-dimethylarsinophenyl)methylarsine]argentio}tetracarbonylcobalt[12] and μ-[2—3-η-(*o*-allylphenyl)dimethylarsine]-bis(nitratosilver).[13] In the former the silver atom is in a distorted tetrahedral environment, being co-ordinated to three As atoms at 2.62(1), 2.62(1), and 2.72(1) Å and to one Co atom at 2.66(1) Å, while in the latter compound only one of the two crystallographically independent Ag atoms, which are both five-co-ordinate, is bonded to an As atom at a rather short distance of 2.488(6) Å. In the present compounds, the Ag–As bond distances increase in a uniform manner depending upon the number of the bulky $AsPh_3$ groups bonded to Ag. It is interesting to note that, if we exclude the unexpected anomalously long bond of 2.678(2) Å in (**3**), the average Ag–As bond distance, *d*, calculated for each of the four cases, varies linearly with the number of the $AsPh_3$ groups (*n*). The equation of the straight line is $d = 2.398(9) + 0.069(3)n$; coefficient of determination, $\tau^2\{=[a\Sigma y_i + b\ \Sigma x_i y_i - \frac{1}{n}\ (\Sigma y_i)^2]/[\Sigma(y_i^2) - \frac{1}{n}\ (\Sigma y_i)^2];\ y = a + bx, n = \text{number of observations}\} = 0.991$.

The co-ordination polyhedra in the three $Ag(AsPh_3)_n(NO_3)$ derivatives are difficult to describe in terms of the localized environments about the metal atoms, as all the compounds show large distortions from the ideal geometries, the angles at Ag being in the ranges 48.0(2)—146.5(4), 49.5(2)—134.2(1), and 43.8(4)—126.0(4)°, for (**1**), (**2**), and (**3**), respectively. Moreover, in all these compounds the distances between the silver atom and the oxygen nitrate atoms span a considerable range of values and this makes it difficult to establish if some of these distances can be considered as more than close contacts. On the other hand, the spread from short to rather long values does not seem unusual for these bonds, when compared with similar bonds involving metal atoms and nitrate oxygen atoms.

In (**1**) (Figure 1) the silver atom is surrounded by the triphenylarsine moiety, with an Ag–As bond of 2.471(2) Å, by a symmetrically bidentate nitrate bonded through O(1) and O(3) [Ag–O 2.560(6) and 2.618(8) Å], and by an adjacent nitrate group which behaves as bidentate in a highly asymmetrical manner: Ag–O(2^i) 2.355(6), Ag–O(1^i) 2.829 (6) Å. All the three oxygen atoms of the nitrate group are involved in co-ordination to silver and the nitrate can be considered as a doubly, symmetrically and asymmetrically, bidentate ligand. The silver environment as well as the ligand behaviour of the NO_3 group are identical to those observed in the related compound $Ag(PPh_3)(NO_3)$.[14] In (**1**), a possible sixth Ag co-ordination site is

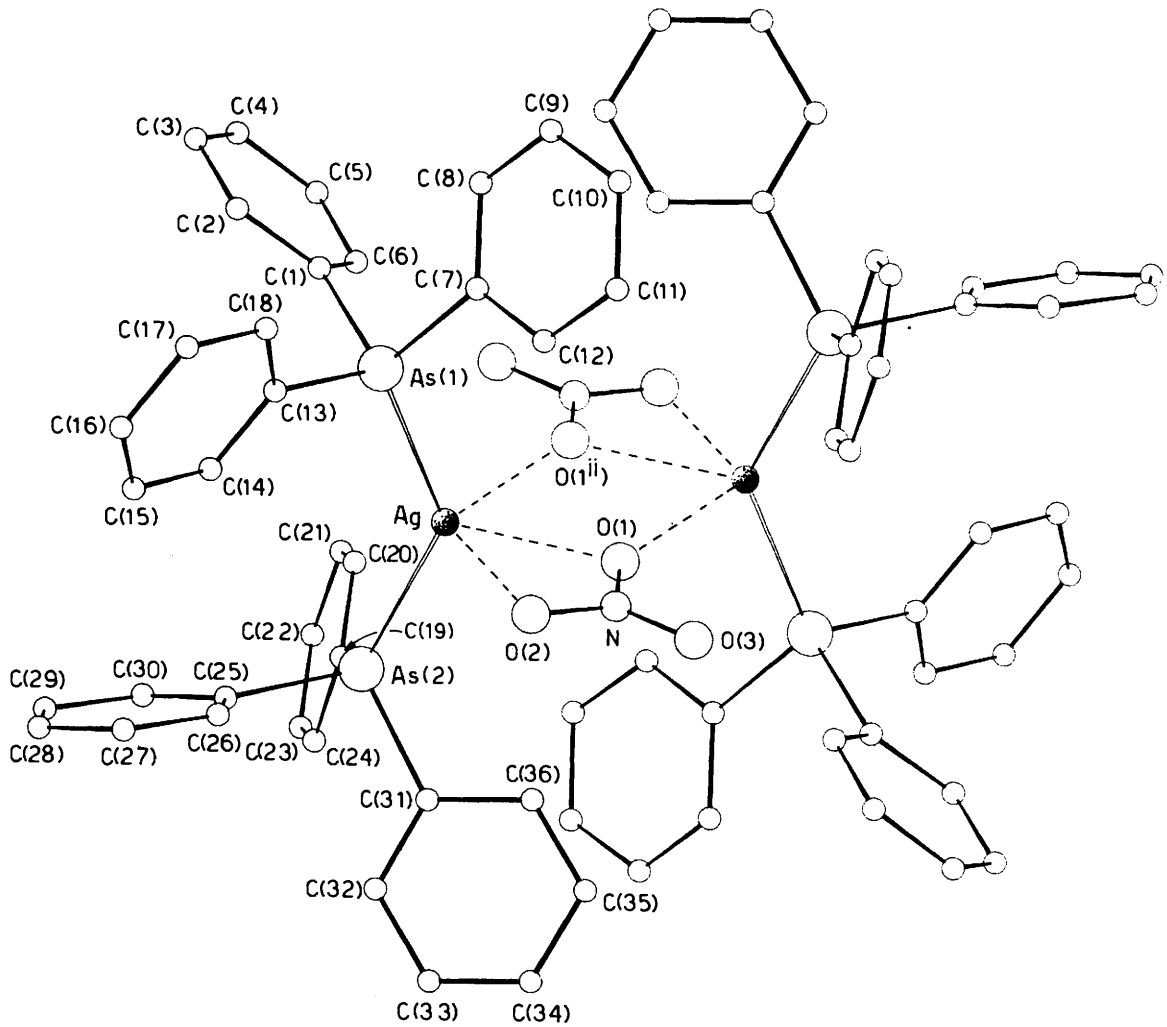

Figure 2. Molecular structure of $Ag(AsPh_3)_2(NO_3)$ (2)

filled through a long-range interaction with a phenyl carbon atom from a neighbouring molecule, $Ag \cdots C(9^{ii})$ 2.985(8) Å. If both the two loosely bonded atoms, namely $O(1^{i})$ and $C(9^{ii})$, are considered as being part of the co-ordination sphere, then the configuration about silver can be described as a severely distorted octahedron.

In (2) (Figure 2) the silver atom is five-co-ordinated by two As atoms from the two $AsPh_3$ moieties, with Ag–As bond distances of 2.535(5) and 2.521(3) Å, and by three O atoms from two symmetry-related NO_3 ions [Ag–O(1) 2.409(6), Ag–O(2) 2.684(7), Ag–$O(1^{ii})$ 2.737(6) Å]. The nitrate ligand is bidentate with one O atom, O(1), bridging asymmetrically two Ag atoms related by a centre of symmetry. This structural situation closely resembles that found in di-μ-nitrato-tetrakis(trimethyl phosphite)disilver.[15]

The co-ordination polyhedron of (3) (Figure 3) is more regular and this is undoubtedly due to the presence of only one nitrate group symmetrically bonding to Ag through O(1) and O(2) with distances of 2.607(16) and 2.544(14) Å, respectively. Silver co-ordination involves also the three As atoms from three $AsPh_3$ groups at distances of 2.608(3), 2.617(2), and 2.678(2) Å.

In all these compounds the As atoms are tetrahedrally surrounded each by one Ag and three C atoms. The distortion of the tetrahedral configuration is as expected, with the Ag-As-C angles significantly larger and the C-As-C angles significantly narrower than the ideal tetrahedral value. The As–C bonds in the three compounds are of similar length, the ranges being 1.931(7)—1.941(8) in (1), 1.928(7)—1.948(7) in (2), and 1.934(11)—1.973(10) Å in (3), and close to those reported for similar compounds.

The crystal packing in these compounds is significantly different and deserves comment. In (1) the bridging behaviour of the nitrate group is such as to generate a polymeric structure through zigzag chains running along the *z* axis, while in (2) the bridging co-ordination of the nitrate causes the formation of dimers. Finally, the crystal structure of (3) contains monomeric units packed with no intermolecular contact <3.35 Å.

The crystal structure of (4) and (5) is built up of discrete well separated ions: the $[Ag(AsPh_3)_4]^+$ cation (Figure 4), which is the same in both compounds, and the anion, which differs: $[SnPh_2(NO_3)_3]^-$ in (4) (Figure 5) and $[SnPh_2(NO_3)_2Cl]^-$ in (5) (Figure 6). In the cation the co-ordination geometry around the silver atom is a regular tetrahedron, the co-ordination sites being occupied by four As atoms, with As–Ag–As angles not departing from the ideal 109.5° value by more than 5°. The Ag–As bonds are essentially equal in length in the two compounds, ranging from 2.643(4) to 2.700(5) Å in (4) and from 2.657(3) to 2.698(3) Å in (5). Unfortunately, as mentioned above, a direct comparison with literature data of the structural dimensions of this cation is not possible. In the anion of (5) the Cl^- ion is partially replaced by an NO_3^- group, with occupancy factors of *ca.* 0.8 for Cl^- and 0.2 for NO_3^-. Only

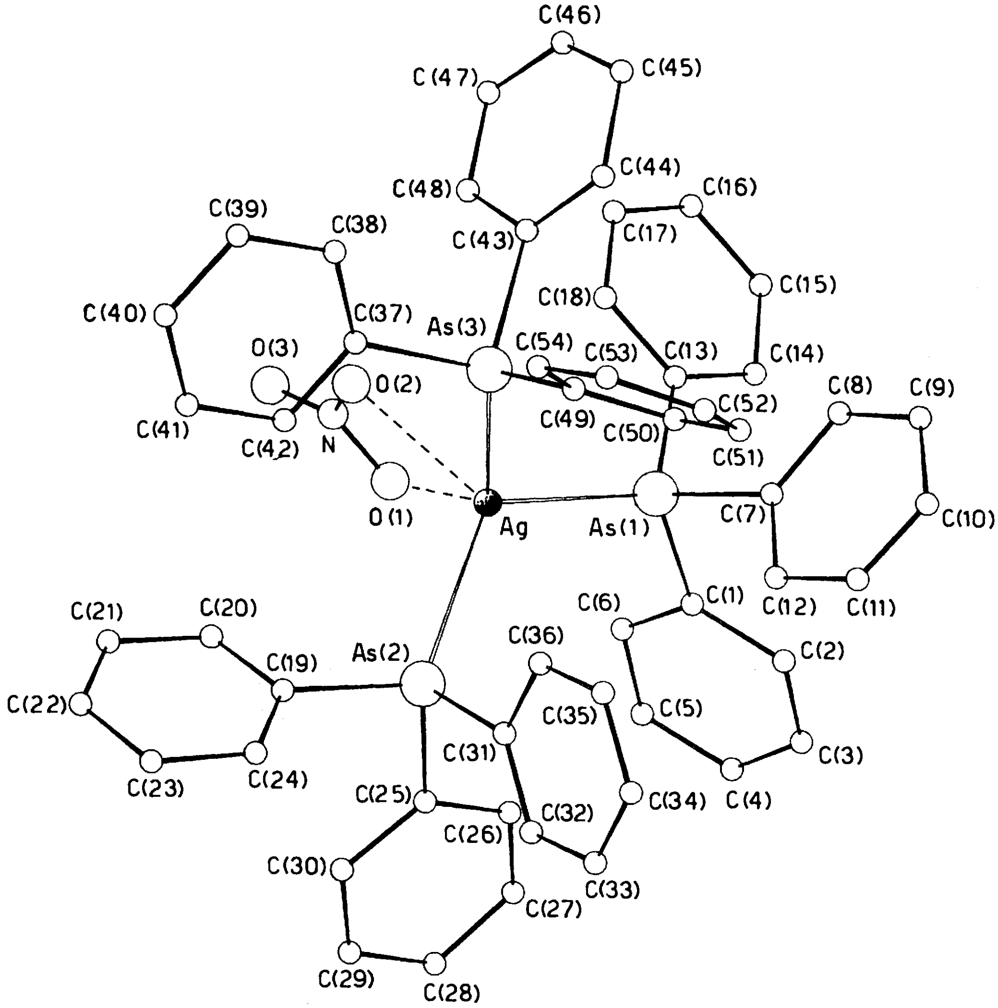

Figure 3. Molecular structure of $Ag(AsPh_3)_3(NO_3)$ (3)

Table 8. Selected bond distances (Å) and angles (°) in the complexes $[Ag(AsPh_3)_4][SnPh_2(NO_3)_2X]$ (4) and (5)

(*a*) In the cation

	(4)	(5)
Ag–As(1)	2.668(3)	2.662(3)
Ag–As(2)	2.700(5)	2.698(3)
Ag–As(3)	2.670(4)	2.687(3)
Ag–As(4)	2.643(4)	2.657(3)
As(1)–C(1)	1.95(2)	1.96(1)
As(1)–C(7)	1.93(2)	1.94(1)
As(1)–C(13)	1.97(1)	1.95(1)
As(2)–C(19)	1.94(2)	1.96(1)
As(2)–C(25)	1.95(2)	1.95(1)
As(2)–C(31)	1.96(1)	1.95(1)
As(3)–C(37)	1.95(2)	1.93(1)
As(3)–C(43)	1.99(2)	1.95(2)
As(3)–C(49)	1.95(1)	1.96(1)
As(4)–C(55)	1.96(2)	1.93(1)
As(4)–C(61)	1.95(1)	1.93(1)
As(4)–C(67)	1.94(2)	1.93(1)
As(1)–Ag–As(2)	114.1(3)	113.2(2)
As(1)–Ag–As(3)	104.6(3)	105.9(2)
As(1)–Ag–As(4)	106.5(3)	106.8(2)
As(2)–Ag–As(3)	110.7(3)	110.0(2)
As(2)–Ag–As(4)	108.8(3)	109.1(2)
As(3)–Ag–As(4)	112.1(3)	111.8(2)
Ag–As(1)–C(1)	116.4(7)	117.0(5)
Ag–As(1)–C(7)	107.9(6)	108.4(4)
Ag–As(1)–C(13)	124.4(6)	122.7(5)
Ag–As(2)–C(19)	113.1(6)	114.6(4)
Ag–As(2)–C(25)	118.6(6)	117.4(4)
Ag–As(2)–C(31)	119.0(6)	118.9(4)
Ag–As(3)–C(37)	112.6(6)	112.2(4)
Ag–As(3)–C(43)	117.2(7)	119.9(4)
Ag–As(3)–C(49)	119.0(6)	117.7(4)
Ag–As(4)–C(55)	117.7(7)	116.8(5)
Ag–As(4)–C(61)	112.3(7)	114.9(4)
Ag–As(4)–C(67)	119.1(6)	117.6(4)
C(1)–As(1)–C(7)	100.6(9)	101.5(6)
C(1)–As(1)–C(13)	103.2(8)	102.8(6)
C(7)–As(1)–C(13)	100.9(8)	101.6(6)
C(19)–As(2)–C(25)	101.7(9)	101.8(6)
C(19)–As(2)–C(31)	102.3(8)	101.6(5)
C(25)–As(2)–C(31)	99.3(8)	99.7(5)
C(37)–As(3)–C(43)	101.6(9)	100.7(6)
C(37)–As(3)–C(49)	101.7(8)	102.4(5)
C(43)–As(3)–C(49)	102.1(9)	101.1(5)
C(55)–As(4)–C(61)	101.1(8)	101.1(5)
C(55)–As(4)–C(67)	103.0(9)	102.7(6)
C(61)–As(4)–C(67)	100.7(9)	101.3(6)

(*b*) In the anion

	(4)	(5)
Sn–O(1)	2.44(2)	2.26(1)
Sn–O(2)	2.34(1)	2.65(1)
Sn–O(4)	2.41(2)	2.69(1)
Sn–O(5)	2.42(2)	2.31(1)
Sn–O(7)	2.30(2)	—

Table 8 (*continued*)

(*b*) In the anion

	(4)	(5)		(4)	(5)
Sn–O(8)	2.60(1)	—	O(8)–Sn–O(7)	49.9(6)	—
Sn–Cl	—	2.443(5)	O(7)–Sn–O(1)	65.3(6)	—
Sn–C(73)	2.09(2)	2.13(2)	O(5)–Sn–Cl	—	85.2(5)
Sn–C(79)	2.12(2)	2.14(2)	Cl–Sn–O(1)	—	85.5(4)
			Sn–O(1)–N(1)	89(1)	104(1)
C(73)–Sn–C(79)	176.3(9)	159.3(7)	Sn–O(2)–N(1)	95(1)	85(1)
O(1)–Sn–O(2)	53.2(6)	50.2(4)	Sn–O(4)–N(2)	93(1)	86(1)
O(2)–Sn–O(4)	72.6(6)	91.2(7)	Sn–O(5)–N(2)	90(1)	102(1)
O(4)–Sn–O(5)	53.9(6)	48.0(4)	Sn–O(7)–N(3)	103(1)	—
O(5)–Sn–O(8)	65.4(6)	—	Sn–O(8)–N(3)	91(1)	—

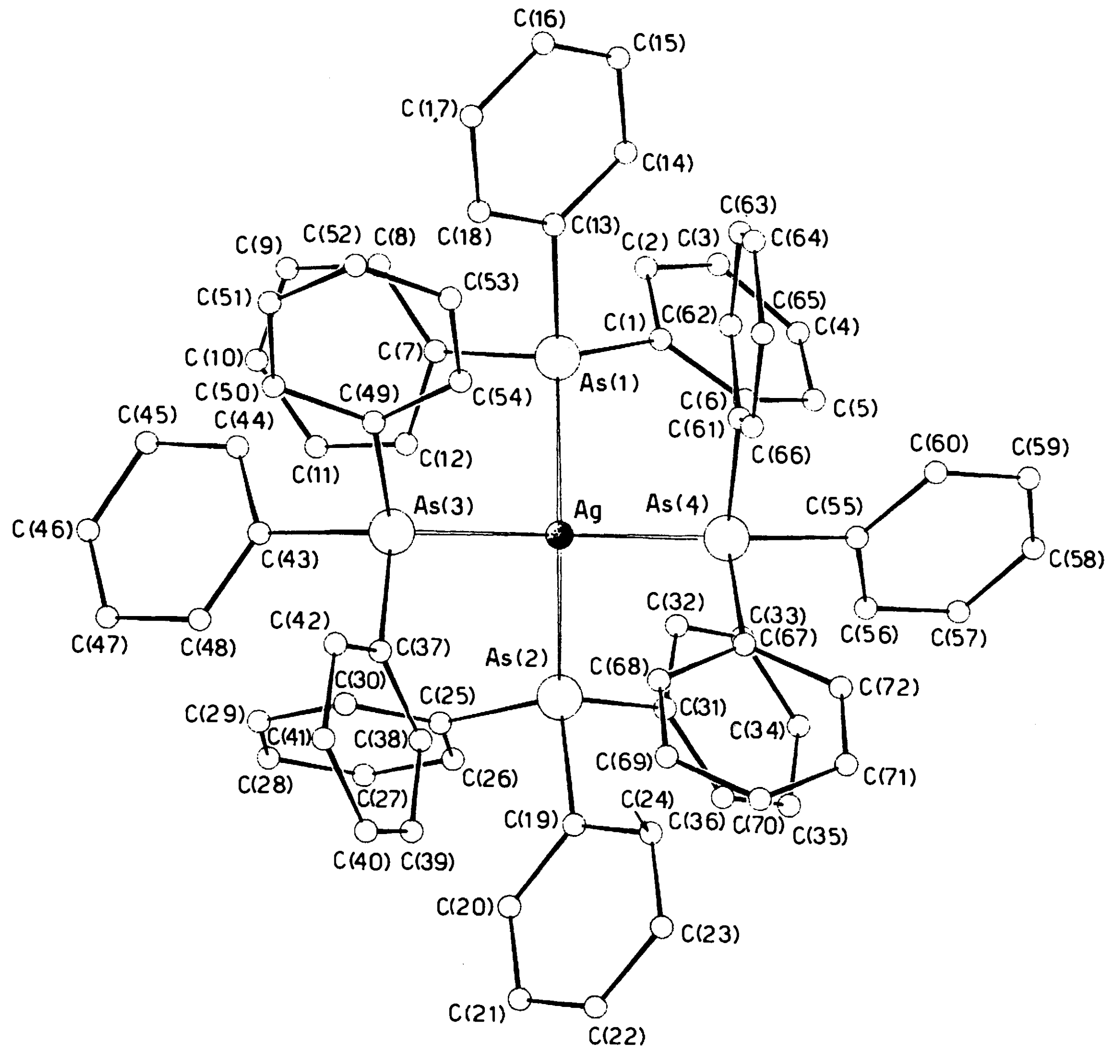

Figure 4. The $[Ag(AsPh_3)_4]^+$ cation present in both (**4**) and (**5**)

two atoms of the latter group were located in the ΔF map, but they were not considered in the calculations and their co-ordinates are therefore not quoted in Table 6. It can be added that in the analogous phosphorus derivative[16] the two partial ligands are statistically interchangeable with a 50% occupancy factor. In (**4**) the co-ordination about tin is hexagonal bipyramidal, while in (**5**) the metal has pentagonal bipyramidal co-ordination. In each case the apical positions are occupied by the two phenyl rings. The tin atom and the surrounding hexagon or pentagon of donor atoms are nearly coplanar, the largest distance to the mean weighted least-squares plane centred on tin being 0.14 and 0.09 Å in (**4**) and (**5**), respectively. In each girdle the O–Sn–O angles are *ca.* 51° within the chelate ring and >65° outside. As shown in Table 8, there seems to be no significant difference between most of the comparable bond distances and angles in the two isostructural compounds. The major difference involves the axial C–Sn–C group, which is almost linear in (**4**) [176.3(9)°], while is significantly bent in (**5**) with an angle of 159.3(7)°. This bending can probably be ascribed to intramolecular C $\cdots$ Cl contacts (3.4—3.5 Å). A

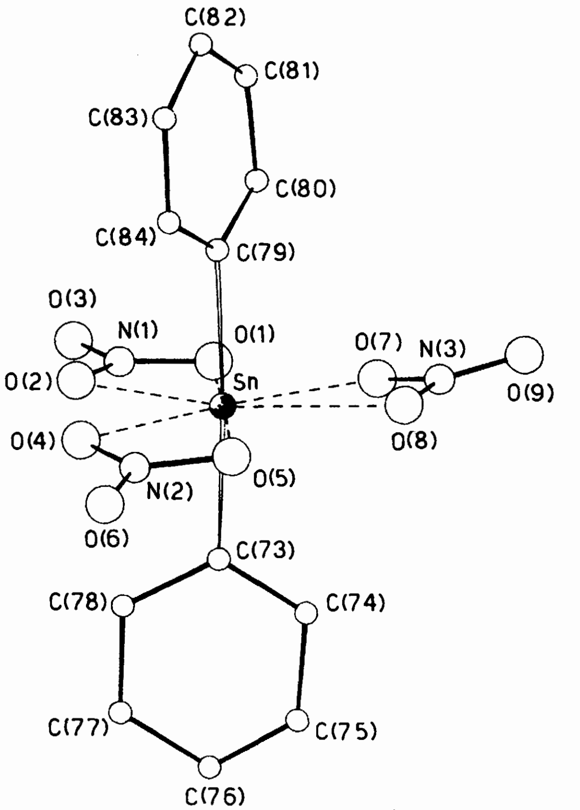

Figure 5. The $[SnPh_2(NO_3)_3]^-$ anion present in (**4**)

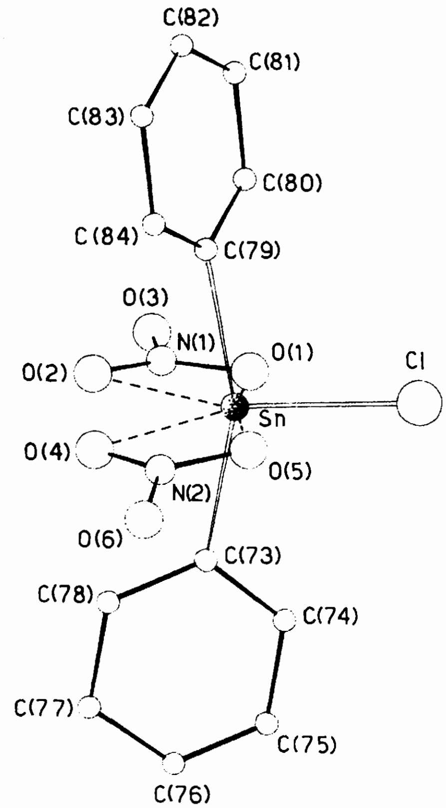

Figure 6. The $[SnPh_2(NO_3)_2Cl]^-$ anion present in (**5**)

second distinctive feature for the two structures is the ligand behaviour of the nitrate groups, in particular as far as the O–Sn bonds are concerned, even though all the nitrates in both (**4**) and (**5**) are bidentate. In fact while the two NO_3^- groups present in (**5**) bind the tin atom in a similar strongly asymmetrical manner [Sn–O(1) 2.26(1), Sn–O(2) 2.65(1); Sn–O(4) 2.69(1), Sn–O(5) 2.31(1) Å], of the three NO_3^- groups occurring in (**4**), one binds the metal symmetrically [Sn–O(4) 2.41(2), Sn–O(5) 2.42(2) Å], the second is to a slight extent asymmetrically bidentate [Sn–O(1) 2.44(2), Sn–O(2) 2.34(1) Å] and the third is strongly asymmetric [Sn–O(7) 2.30(2), Sn–O(8) 2.60(1) Å].

No intermolecular contacts shorter than the sum of van der Waals radii occur between the anions and cations in the two compounds. The closest approach is 3.22(2) Å in (**4**) [3.34(2) Å in (**5**)] between O(2) and C(65) at $1 - x, \bar{y}, 1 - z$.

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