Synthesis and Structural Studies on Silver–Tin Complex Salts with Bis(diphenylarsino)methane and Bis(diphenylphosphino)methane†

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Three new silver–tin complex salts with bis(diphenylarsino)methane (dpam) and bis(diphenylphosphino)methane (dppm) have been synthesized. The i.r. and ^{31}P and ^{119}Sn n.m.r. spectra as well as the conductivity data are reported and discussed together with the *X*-ray crystal structure of one of them, namely $[Ag_3Cl_2(dppm)_3][SnPh_2(NO_3)_2Cl]\cdot CH_3OH$. The trinuclear silver complex contains bridging chlorine and dppm ligands. All the three independent silver atoms are four-co-ordinated in a distorted tetrahedral configuration involving two chlorine and two phosphorus atoms. The co-ordination polyhedron about tin can be described as a distorted pentagonal bipyramid, having a chlorine atom and four nitrate oxygen atoms in the equatorial plane and two phenyl carbons at the apices.

In earlier papers we have described the synthesis and the spectroscopic and *X*-ray diffractometric characterization of silver–tin complex salts containing arsines or phosphines as ligands.[1–4] These compounds are of interest because of the joint presence of silver and tin as well as their ionic nature. To date, compounds consisting of discrete $[AgL_n]^+$ cations (n = 2, L = diphosphine; n = 4, L = monoarsine or monophosphine) and $[SnPh_{4-x}(NO_3)_xX]^-$ anions (x = 1, X = NO$_3$; x = 2, X = Cl or NO$_3$) have been studied in our laboratories.

In order to obtain further information on the nature and stereochemistry of this kind of compound we have extended our investigation using as ligands bis(diphenylarsino)methane (dpam) and bis(diphenylphosphino)methane (dppm).

The present work deals with the synthesis, i.r., and ^{31}P and ^{119}Sn n.m.r. spectroscopic properties of new silver–tin complex salts with dpam and dppm. Also described is the crystal and molecular structure of one of these compounds, $[Ag_3Cl_2(dppm)_3][SnPh_2(NO_3)_2Cl]\cdot CH_3OH$, in which the silver cation interestingly shows a trinuclear nature.

Experimental

Reagents.—All reagents and solvents were reagent grade; the solvents were dried by standard techniques. The compounds $SnPh_3Cl$, $SnPh_2Cl_2$, $AgNO_3$, dpam, and dppm were used as supplied commercially without further purification; $SnPh_2(NO_3)_2$ and $SnPh_3(NO_3)$ were prepared as previously described.[4–6]

$[Ag(dpam)_2(NO_3)]$. Silver nitrate and dpam (1:2 molar ratio) were dissolved in a methanol–acetone (1:1 v/v) mixture. The solution was stirred at room temperature for 1 h and then concentrated on a rotary evaporator until crystallization began. Recrystallization was from methanol.

$[\{Ag(dppm)(NO_3)\}_2]$. The dimeric complex was prepared using the procedure of Ho and Bau,[7] and recrystallized from hot (40—50 °C) methanol.

Preparation of Silver–Tin Complex Salts.—$[Ag(dpam)_2][SnPh_2(NO_3)_3]$ *and* $[Ag(dppm)_2][SnPh_2(NO_3)_3]$. The following general procedure was used for both compounds. An acetone solution of dpam (or dppm) was added under N_2 atmosphere at room temperature to a solution of $SnPh_2(NO_3)_2$ and $AgNO_3$ (2:1:1 molar ratio) in acetonitrile–acetone (1:1 v/v). The solution was stirred for about 1 h. By slow evaporation of the solvents, a white microcrystalline product was isolated. Yield 85%.

Both compounds can be also obtained by reacting $SnPh_2(NO_3)_2$ with $[Ag(dpam)_2(NO_3)]$ or $[\{Ag(dppm)(NO_3)\}_2]$ in acetonitrile–acetone (3:2 v/v).

Interestingly, for the preparation of $[Ag(dppm)_2][SnPh_2(NO_3)_3]$ a third procedure can be used, which is as follows. $SnPh_2(NO_3)_2$ (3 mmol) and dppm (6 mmol), dissolved in chloroform (60 cm^3), were added to $AgNO_3$ (3 mmol) dissolved in deoxygenated water (60 cm^3). The mixture was vigorously shaken for *ca.* 5 h under an N_2 atmosphere at room temperature, and the aqueous layer removed. A quantitative analysis of silver and tin, carried out on the aqueous layer, revealed the complete absence of silver and the presence of a small amount (*ca.* 5%) of tin [$SnPh_2(OH)_2$ was found as partial hydrolysis product of the tin reagent]. The original chloroform solution was filtered and concentrated on a rotary evaporator almost to dryness. The resulting solid was recrystallized from methanol to give white crystals of the above silver–tin complex salt. Yield 80%.

$[Ag_3Cl_2(dppm)_3][SnPh_2(NO_3)_2Cl]\cdot CH_3OH$. $[\{Ag(dppm)(NO_3)\}_2]$ and $SnPh_2Cl_2$ (1:1 molar ratio) were dissolved in acetonitrile–methanol (1:1 v/v) and the mixture stirred for 1 h. White needle-shaped crystals were formed on standing. Yield 80%. No precipitation of silver chloride was observed. No identification was made for other tin species remaining in solution, however the unreacted tin reagent probably undergoes partial hydrolysis (or solvolysis) as is typical for these compounds.

Measurements.—Microanalyses (C, H, and N) were made on a Perkin-Elmer 240 automatic instrument. Determination for silver and tin was by atomic absorption spectroscopy on a Perkin-Elmer 303-HGA 70 instrument, using a procedure previously described.[4] The i.r. spectra were recorded as KBr

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† A preliminary account of this work was given at the 5th International Conference on the Organometallic and Co-ordination Chemistry of Germanium, Tin, and Lead, Padua (Italy), September 1986.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Analytical (%)[a] and conductivity data

Compound	C	H	N	Sn	Ag	$\Lambda_M{}^b$/ohm^{-1} cm^2 mol^{-1}
$[\{Ag(dppm)(NO_3)\}_2]$	54.35 (54.15)	4.25 (4.00)	2.80 (2.55)		20.20 (19.45)	
$[Ag(dppm)_2][SnPh_2(NO_3)_3]$	55.25 (55.75)	4.10 (4.10)	3.10 (3.15)	7.90 (8.90)	9.10 (8.10)	15.80
$[Ag_3Cl_2(dppm)_3][SnPh_2(NO_3)_2Cl]\cdot CH_3OH$	52.70 (52.75)	3.90 (3.85)	1.50 (1.40)	6.90 (6.00)	16.20 (16.35)	11.90
$[Ag(dpam)_2(NO_3)]$	54.20 (53.90)	4.10 (4.00)	1.40 (1.25)		10.50 (9.70)	
$[Ag(dpam)_2][SnPh_2(NO_3)_3]$	48.40 (49.25)	3.55 (3.60)	2.40 (2.80)	6.90 (7.85)	8.20 (7.15)	10.43

[a] Calculated values in parentheses. [b] 10^{-3} mol dm^{-3} solutions.

discs using a Perkin-Elmer 283 B spectrophotometer over the range 4 000—200 cm^{-1}. Tin-119 and ^{31}P-$\{^1$H$\}$ n.m.r. spectra were recorded on a Bruker CXP 200 instrument at 74.5 and 81.0 MHz respectively, using ^{2}H lock. Chemical shifts are given relative to external $SnMe_4$ and 85% H_3PO_4 respectively; a positive sign indicates a shift to low field of the resonance. [^{2}H]Chloroform or [^{2}H$_6$]acetone were used as solvents. Conductivity measurements were made on a Philips PW 9504/00 bridge in nitrobenzene (10^{-3} mol dm^{-3} at 25 °C). Analytical and conductivity data are given in Table 1.

Crystallography of $[Ag_3Cl_2(dppm)_3][SnPh_2(NO_3)_2Cl]\cdot CH_3OH$.—*Crystal data.* $C_{88}H_{80}Ag_3Cl_3N_2O_7P_6Sn$, M = 2 012.10, monoclinic, a = 39.822(16), b = 10.603(2), c = 20.554(14) Å, β = 91.27(5)°, U = 8 676(7) Å^3 (by least-squares refinement on diffractometer angles for 30 automatically centred reflections, λ = 1.514 78 Å), space group $P2_1/a$ (no. 14) from systematic extinctions, D_m = 1.58 g cm^{-3}, Z = 4, D_c = 1.540 g cm^{-3}, μ(Cu-K_α) = 101.48 cm^{-1}.

Data collection and processing. Siemens AED three-circle diffractometer in conjunction with a General Automation Jumbo 220 computer, $\theta/2\theta$ mode with nickel-filtered Cu-K_α radiation.* 16 076 Reflections measured ($3 \leqslant \theta \leqslant 65°$, $\pm h$ $+k$ $+l$), 15 344 unique, giving 8 165 with $I \geqslant 2\sigma(I)$. Slight crystal decay (*ca.* 12%) corrected during processing. Individual reflection profiles analysed following a modified version of the Lehmann and Larsen procedure.[8] Data corrected for Lorentz and polarization factors and for absorption using the empirical method of Walker and Stuart.[9]

Structure solution and refinement. The positions of the tin and three silver atoms were obtained from the best E map computed with the automatic direct methods subroutine in MULTAN.[10] These positions were also checked against a Patterson map. A Fourier synthesis based on the silver and the tin phases revealed all the non-hydrogen atoms belonging to the cationic and anionic moieties. The structure was refined by using a full-matrix least-squares procedure minimizing the function $\Sigma w(|F_o| - |F_c|)^2$. All atoms heavier than carbon were given anisotropic thermal parameters, while the carbon atoms were restricted to isotropic motion. Rigid-body constraints were applied to the phenyl rings. A difference map calculated at the final stages of refinement revealed, with some difficulty, the presence of a solvent molecule which was recognized as methanol and refined isotropically. Due to the large number of variables, the refinement was carried out by blocking the atoms into two groups. All the hydrogen atoms from the phenyl rings were included at calculated positions (C–H 1.08 Å) in the last refinement cycle. The final residual indices for 352 variables refined against 8 165 data were R = 0.0748, R' = 0.0963, and goodness of fit = 1.2381 with weights $w = 1.1133/[\sigma^2(F_o) + 0.003\,210\,F_o{}^2]$. The final difference-Fourier map showed some rather larger positive peaks (1.3 e Å^{-3}) around the Ag positions.

Throughout the analysis atomic scattering factors for neutral atoms were used. The calculations included both $\Delta f'$ and $\Delta f''$ corrections for the anomalous dispersion effects of the heavy atoms. Computations were performed on Cray X-MP/12 and GOULD 32/77 computers, using the programs of the SHELX 76 package.[11] The other programs used in the structure determination have been cited elsewhere.[12]

The final atomic co-ordinates are listed in Table 2, and relevant bond distances and angles are given in Table 3. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

This work provides further evidence of the importance of the nature and geometry of the arsine or phosphine ligand to obtain silver–tin complex salts.[2,4] In fact, while *cis*-1,2-bis(diphenylphosphino)ethene (cdppet), bis(diphenylarsino)methane (dpam), and bis(diphenylphosphino)methane (dppm), which are well suitable for producing stable chelate rings, led to the isolation of silver–tin complexes, attempts to prepare this kind of compound using 1,2-bis(diphenylarsino)ethane, 1,3-bis(diphenylphosphino)propane, and 1,4-bis(diphenylphosphino)butane, under similar experimental conditions, were unsuccessful. Moreover, it is worth noting that while cdppet produces silver–tin complex salts with diphenyl- as well as with triphenyl-tin derivatives, when dpam or dppm are used the reaction only occurs with diphenyltin derivatives.

X-*Ray Structure of* $[Ag_3Cl_2(dppm)_3][SnPh_2(NO_3)_2Cl]\cdot CH_3OH$.—The crystal structure consists of $[Ag_3Cl_2(dppm)_3]^+$ cations, $[SnPh_2(NO_3)_2Cl]^-$ anions, and molecules of methanol of crystallization. ORTEP diagrams and atom labelling schemes for cation and anion are given in Figures 1 and 2, respectively. The complex cation is a trinuclear one, whose overall structure may be described as a triangular array of silver atoms bridged by chlorine and dppm ligands. The same trinuclear formulation was previously reported for the related cation $[Ag_3Br_2(dppm)_3]^+$.[13] There is no imposed crystallographic symmetry, but the skeletal atoms of the cation show a

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* The choice of the radiation used for data collection deserves some comments. Initially, the data set was collected by using the same crystal with Mo-K_α radiation (more suitable for a sample of such a chemical composition), but the results were not satisfactory: the data could not be refined below an R index of 0.09 and the estimated standard deviations of the atomic co-ordinates were 1.5—2.0 times larger than those obtained by using Cu-K_α radiation. These findings can partially be explained taking into consideration that a short-wave radiation such as Mo-K_α does not give a good separation between the reflections when one or more unit-cell edges (in this case a) are of considerable length. Moreover, the use of Mo-K_α radiation led to a lower number of observed reflections. However, we have noted that the corresponding structural parameters observed for the two data sets are fully comparable.

Table 2. Fractional atomic co-ordinates ($\times 10^5$ for Ag and Sn, and $\times 10^4$ for Cl, P, O, N, and C)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ag(1)	59 905(2)	15 341(10)	15 516(4)	C(34)	7 089(2)	3 464(8)	3 889(4)
Ag(2)	65 687(2)	34 900(10)	24 096(4)	C(35)	7 197(2)	3 778(8)	4 519(4)
Ag(3)	60 064(2)	19 982(10)	31 867(4)	C(36)	7 456(2)	3 099(8)	4 822(4)
Sn	66 141(2)	55 930(10)	74 689(4)	C(37)	7 608(2)	2 106(8)	4 495(5)
Cl(1)	5 868(1)	3 762(3)	2 274(2)	C(38)	7 501(2)	1 792(8)	3 865(4)
Cl(2)	6 474(1)	971(3)	2 423(2)	C(39)	7 241(2)	2 471(8)	3 562(4)
Cl(3)	7 118(1)	4 413(5)	7 592(2)	C(40)	5 854(2)	3 383(10)	4 717(4)
P(1)	6 186(1)	2 578(3)	560(1)	C(41)	5 745(2)	4 611(10)	4 833(4)
P(2)	6 762(1)	4 163(3)	1 316(1)	C(42)	5 467(2)	4 819(10)	5 222(4)
P(3)	6 752(1)	4 312(3)	3 472(1)	C(43)	5 299(2)	3 799(10)	5 493(4)
P(4)	6 203(1)	2 973(3)	4 200(2)	C(44)	5 408(2)	2 571(10)	5 377(4)
P(5)	5 552(1)	439(3)	3 217(1)	C(45)	5 685(2)	2 363(10)	4 988(4)
P(6)	5 547(1)	−53(2)	1 735(2)	C(46)	6 471(2)	2 031(9)	4 747(4)
O(1)	6 725(3)	5 332(10)	6 393(5)	C(47)	6 604(2)	902(9)	4 519(4)
O(2)	6 264(3)	6 473(10)	6 383(5)	C(48)	6 796(2)	137(9)	4 935(4)
O(3)	6 518(3)	6 121(11)	5 488(6)	C(49)	6 855(2)	502(9)	5 580(4)
O(4)	6 643(3)	5 527(11)	8 581(5)	C(50)	6 722(2)	1 631(9)	5 808(4)
O(5)	6 188(3)	6 585(12)	8 350(6)	C(51)	6 530(2)	2 396(9)	5 392(4)
O(6)	6 370(4)	6 269(16)	9 369(8)	C(52)	5 623(2)	−575(7)	3 927(3)
O(7)	4 235(6)	3 881(22)	6 908(11)	C(53)	5 938(2)	−1 143(7)	3 986(3)
N(1)	6 504(3)	5 973(12)	6 082(6)	C(54)	6 023(2)	−1 836(7)	4 543(3)
N(2)	6 384(4)	6 207(13)	8 774(7)	C(55)	5 792(2)	−1 962(7)	5 040(3)
C(1)	6 396(3)	4 109(11)	681(5)	C(56)	5 477(2)	−1 394(7)	4 981(3)
C(2)	6 429(3)	4 465(11)	4 074(5)	C(57)	5 392(2)	−701(7)	4 424(3)
C(3)	5 539(3)	−740(11)	2 556(5)	C(58)	5 127(2)	1 035(8)	3 275(4)
C(4)	5 830(2)	3 051(8)	33(4)	C(59)	5 093(2)	2 335(8)	3 354(4)
C(5)	5 880(2)	3 568(8)	−581(4)	C(60)	4 774(2)	2 874(8)	3 382(4)
C(6)	5 605(2)	3 989(8)	−955(4)	C(61)	4 489(2)	2 112(8)	3 333(4)
C(7)	5 281(2)	3 894(8)	−714(4)	C(62)	4 523(2)	812(8)	3 254(4)
C(8)	5 232(2)	3 378(8)	−99(4)	C(63)	4 842(2)	273(8)	3 225(4)
C(9)	5 507(2)	2 957(8)	275(4)	C(64)	5 116(2)	434(9)	1 575(4)
C(10)	6 449(2)	1 652(8)	26(4)	C(65)	5 026(2)	1 680(9)	1 703(4)
C(11)	6 659(2)	2 170(8)	−439(4)	C(66)	4 692(2)	2 059(9)	1 629(4)
C(12)	6 829(2)	1 383(8)	−865(4)	C(67)	4 448(2)	1 192(9)	1 427(4)
C(13)	6 789(2)	78(8)	−826(4)	C(68)	4 538(2)	−54(9)	1 300(4)
C(14)	6 580(2)	−440(8)	−361(4)	C(69)	4 872(2)	−433(9)	1 374(4)
C(15)	6 410(2)	347(8)	65(4)	C(70)	5 594(2)	−1 448(7)	1 232(3)
C(16)	7 084(2)	3 411(8)	953(4)	C(71)	5 592(2)	−2 672(7)	1 481(3)
C(17)	7 198(2)	2 271(8)	1 214(4)	C(72)	5 640(2)	−3 697(7)	1 068(3)
C(18)	7 475(2)	1 668(8)	948(4)	C(73)	5 690(2)	−3 499(7)	406(3)
C(19)	7 637(2)	2 205(8)	421(4)	C(74)	5 692(2)	−2 274(7)	157(3)
C(20)	7 523(2)	3 345(8)	160(4)	C(75)	5 644(2)	−1 249(7)	570(3)
C(21)	7 246(2)	3 948(8)	426(4)	C(76)	6 770(3)	7 498(8)	7 464(5)
C(22)	6 828(2)	5 842(7)	1 341(4)	C(77)	7 110(3)	7 755(8)	7 565(5)
C(23)	7 157(2)	6 223(7)	1 480(4)	C(78)	7 225(3)	8 998(8)	7 552(5)
C(24)	7 232(2)	7 501(7)	1 555(4)	C(79)	6 999(3)	9 983(8)	7 439(5)
C(25)	6 977(2)	8 398(7)	1 492(4)	C(80)	6 659(3)	9 726(8)	7 338(5)
C(26)	6 647(2)	8 017(7)	1 354(4)	C(81)	6 544(3)	8 484(8)	7 351(5)
C(27)	6 573(2)	6 738(7)	1 278(4)	C(82)	6 240(3)	4 193(11)	7 446(6)
C(28)	6 902(2)	5 930(7)	3 408(4)	C(83)	5 929(3)	4 347(11)	7 132(6)
C(29)	7 233(2)	6 291(7)	3 542(4)	C(84)	5 687(3)	3 397(11)	7 165(6)
C(30)	7 329(2)	7 547(7)	3 466(4)	C(85)	5 757(3)	2 293(11)	7 512(6)
C(31)	7 093(2)	8 442(7)	3 257(4)	C(86)	6 069(3)	2 140(11)	7 826(6)
C(32)	6 762(2)	8 081(7)	3 124(4)	C(87)	6 310(3)	3 089(11)	7 793(6)
C(33)	6 666(2)	6 825(7)	3 199(4)	C(88)	4 606(7)	4 004(27)	6 750(13)

pseudo-three-fold symmetry. The central skeleton corresponds closely to a trigonal bipyramid with the silver atoms in the equatorial and the chlorine atoms in the axial positions. The edges of the triangle are not equivalent, with Ag ··· Ag separations of 3.198(2), 3.396(3), and 3.540(2) Å for Ag(2) ··· Ag(3), Ag(1) ··· Ag(3), and Ag(1) ··· Ag(2), respectively.

The silver atoms are each co-ordinated to two chlorine atoms and two phosphorus atoms, the latter belonging to different dppm molecules, in a severely distorted tetrahedral arrangement. Particularly significant is the enlargement of the P–Ag–P angle [119.1(2)—132.2(2)°], and the narrowing of Cl–Ag–Cl [87.9(2)—90.5(1)°]. These angular distortions appear to be a direct consequence of constraints imposed by the dppm ligand structure.

Each chlorine atom is three-co-ordinate, bridging three metal centres to form four-membered butterfly-shaped Ag_2Cl_2 ring systems. As indicated by the values of the Ag–Cl bonds (Table 3), the co-ordination of Cl(1) to its three related silver atoms is slightly asymmetrical, whereas a higher symmetry is present in the co-ordination of Cl(2). The angles subtended at the chlorine atoms range from 70.9(1) to 82.5(1)°. The Ag–Cl bonds are of unequal lengths, but all the values fall within the range 2.532—

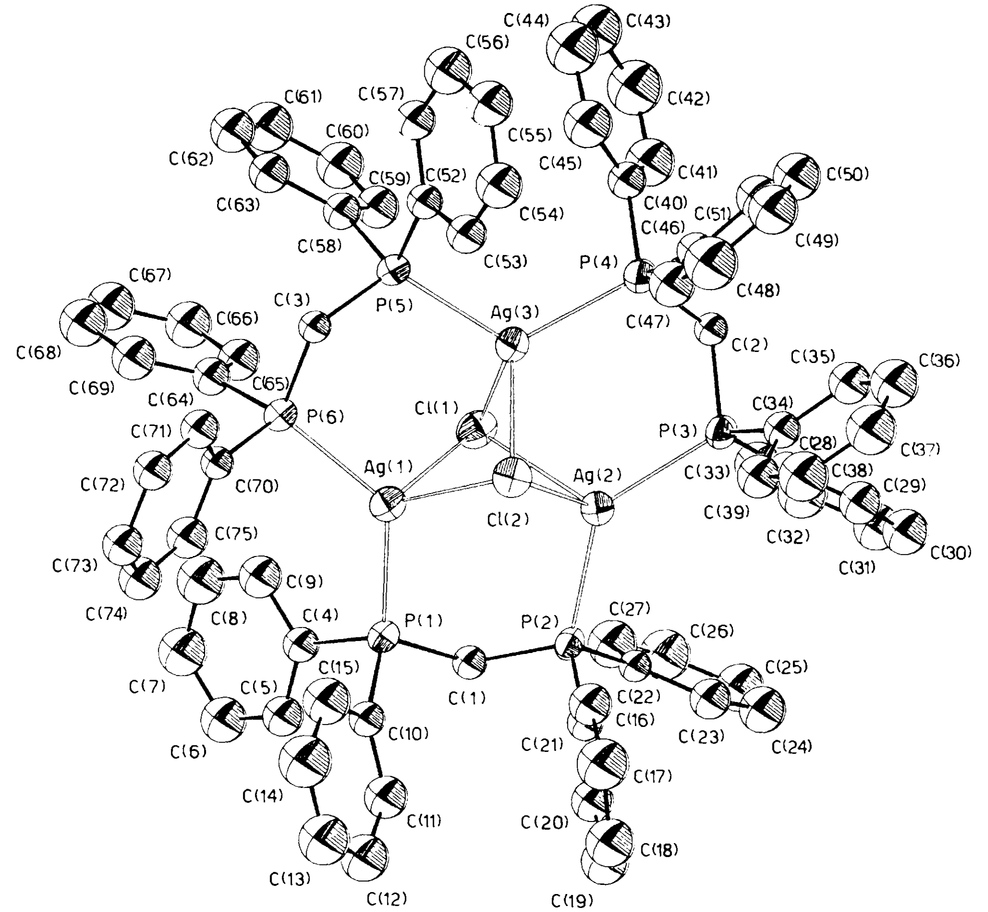

Figure 1. Perspective view of the $[Ag_3Cl_2(dppm)_3]^+$ cation. The ellipsoidal boundaries are at the 40% probability level

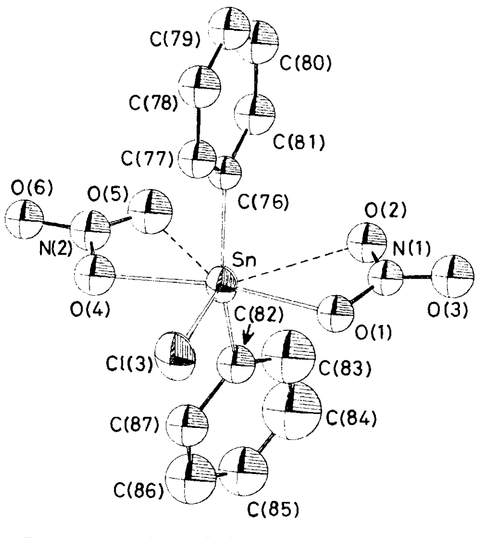

Figure 2. Perspective view of the $[SnPh_2(NO_3)_2Cl]^-$ anion. The ellipsoidal boundaries are at the 30% probability level

2.913 Å, observed in a number of four-co-ordinate silver–chloride bridged systems.[14–21]

The six Ag–P bonds lie in a very narrow range, *i.e.* 2.438(4)—2.474(4) Å and are typical of such distances for silver(I) tetrahedrally surrounded by two P and two Cl ligands: 2.461(4) and 2.481(4) Å in di-μ-[bis(diphenylphosphinoethyl) sulphide]-di-μ-chloro-disilver,[15] 2.472(3)—2.499(4) Å in dimeric [1,5-bis(diphenylphosphino)pentane]chlorosilver,[17] 2.467(2) and 2.472(2) Å in $[\{Ag(PPh_3)_2Cl\}_2]$,[18] and 2.432(3) and 2.452(3) Å in $[Ag_2Cl_2L_3]$ [L = diphenyl(2-pyridyl)phosphine].[19] Only slightly shorter values have been reported for the two other structurally characterized silver(I) dppm complexes, both of which exhibit tetrahedral co-ordination geometry: 2.413(8)—2.459(8) Å in $[Ag_3Br_2(dppm)_3]^+$ [13] and 2.436(2) and 2.417(2) Å in $[Ag_2(dppm)_2(NO_3)_2]$.[7]

By virtue of the bridging action of the chlorine and dppm ligands, six considerably puckered chelate rings, each comprising six atoms (AgClAgPCP), are formed. In all of these, four of the six atoms, namely the two Ag and the two P, are coplanar within 0.07 Å, whereas Cl and C are markedly displaced from the Ag_2P_2 plane [C, 0.69—0.74; Cl(1), 1.90—2.13; Cl(2), 1.64—1.91 Å]. As regards the conformational aspects, three of these rings [Ag(1)Cl(2)Ag(2)P(2)C(1)P(1), Ag(1)Cl(1)Ag(3)-P(5)C(3)P(6), and Ag(2)Cl(2)Ag(3)P(4)C(2)P(3)] adopt a chair conformation, while the other three [Ag(1)Cl(1)Ag(2)P(2)-C(1)P(1), Ag(1)Cl(2)Ag(3)P(5)C(3)P(6), and Ag(2)Cl(1)Ag(3)-P(4)C(2)P(3)], given the geometry, are obviously boat-shaped. In each case the displacement of the Cl atom from the four-atom plane is greater for the boat (mean 2.01 Å) than for the chair (mean 1.79 Å) conformation.

The phosphorus atoms have the expected distortion from tetrahedral symmetry. The 18 Ag–P–C angles, with two exceptions, are all greater than 109.5°, whereas the 18 C–P–C angles are all smaller. The P–C bond distances have normal values, as have the P–C–C angles.

The co-ordination polyhedron about tin is a distorted

Table 3. Selected bond distances (Å) and angles (°)

(*a*) cation

Ag(1)–P(1)	2.462(3)	P(2)–C(16)	1.808(9)	P(3)–C(34)	1.814(9)	Ag(3)–Cl(2)	2.692(4)
Ag(1)–P(6)	2.474(4)	P(2)–C(22)	1.826(8)	P(4)–C(2)	1.841(12)	P(5)–C(3)	1.845(12)
Ag(1)–Cl(1)	2.838(4)	Ag(2)–P(2)	2.454(3)	P(4)–C(40)	1.821(9)	P(5)–C(52)	1.829(8)
Ag(1)–Cl(2)	2.669(4)	Ag(2)–P(3)	2.448(3)	P(4)–C(46)	1.830(10)	P(5)–C(58)	1.815(8)
P(1)–C(1)	1.841(12)	Ag(2)–Cl(1)	2.814(4)	Ag(3)–P(4)	2.438(4)	P(6)–C(3)	1.841(11)
P(1)–C(4)	1.834(8)	Ag(2)–Cl(2)	2.698(3)	Ag(3)–P(5)	2.452(4)	P(6)–C(64)	1.816(8)
P(1)–C(10)	1.821(9)	P(3)–C(2)	1.814(11)	Ag(3)–Cl(1)	2.698(4)	P(6)–C(70)	1.816(8)
P(2)–C(1)	1.832(12)	P(3)–C(28)	1.821(8)				
P(1)–Ag(1)–P(6)	132.2(2)	Ag(2)–P(2)–C(22)	108.6(3)	C(2)–P(3)–C(34)	104.5(5)	Cl(1)–Ag(3)–Cl(2)	90.5(1)
P(1)–Ag(1)–Cl(1)	96.9(1)	C(1)–P(2)–C(16)	104.6(5)	C(28)–P(3)–C(34)	105.2(5)	Ag(3)–P(5)–C(3)	116.6(4)
P(1)–Ag(1)–Cl(2)	114.8(2)	C(1)–P(2)–C(22)	101.9(5)	Ag(3)–P(4)–C(2)	113.2(4)	Ag(3)–P(5)–C(52)	108.5(3)
P(6)–Ag(1)–Cl(1)	110.8(2)	C(16)–P(2)–C(22)	105.3(5)	Ag(3)–P(4)–C(40)	111.4(4)	Ag(3)–P(5)–C(58)	117.2(3)
P(6)–Ag(1)–Cl(2)	104.6(1)	P(2)–Ag(2)–P(3)	129.5(1)	Ag(3)–P(4)–C(46)	117.8(4)	C(3)–P(5)–C(52)	101.0(5)
Cl(1)–Ag(1)–Cl(2)	88.0(1)	P(2)–Ag(2)–Cl(1)	98.8(2)	C(2)–P(4)–C(40)	105.0(5)	C(3)–P(5)–C(58)	105.8(5)
Ag(1)–P(1)–C(1)	115.8(4)	P(2)–Ag(2)–Cl(2)	109.6(1)	C(2)–P(4)–C(46)	106.0(5)	C(52)–P(5)–C(58)	106.2(4)
Ag(1)–P(1)–C(4)	110.9(4)	P(3)–Ag(2)–Cl(1)	109.1(2)	C(40)–P(4)–C(46)	102.4(5)	Ag(1)–P(6)–C(3)	115.9(4)
Ag(1)–P(1)–C(10)	117.0(3)	P(3)–Ag(2)–Cl(2)	112.5(1)	P(4)–Ag(3)–P(5)	119.1(2)	Ag(1)–P(6)–C(64)	117.0(3)
C(1)–P(1)–C(4)	100.4(5)	Cl(1)–Ag(2)–Cl(2)	87.9(2)	P(4)–Ag(3)–Cl(1)	110.9(1)	Ag(1)–P(6)–C(70)	112.7(4)
C(1)–P(1)–C(10)	107.0(5)	Ag(2)–P(3)–C(2)	116.0(4)	P(4)–Ag(3)–Cl(2)	117.2(2)	C(3)–P(6)–C(64)	104.0(5)
C(4)–P(1)–C(10)	103.9(4)	Ag(2)–P(3)–C(28)	111.3(3)	P(5)–Ag(3)–Cl(1)	110.2(2)	C(3)–P(6)–C(70)	101.8(5)
Ag(2)–P(2)–C(1)	116.7(4)	Ag(2)–P(3)–C(34)	116.6(3)	P(5)–Ag(3)–Cl(2)	105.2(1)	C(64)–P(6)–C(70)	103.8(5)
Ag(2)–P(2)–C(16)	118.0(3)	C(2)–P(3)–C(28)	101.7(5)				

(*b*) anion

Sn–O(1)	2.282(10)	Sn–C(82)	2.103(12)	N(1)–O(2)	1.26(2)	N(2)–O(4)	1.33(2)
Sn–O(4)	2.287(11)	Sn–O(2)	2.766(11)	N(1)–O(3)	1.23(2)	N(2)–O(5)	1.22(2)
Sn–Cl(3)	2.374(5)	N(1)–O(1)	1.27(2)	Sn–O(5)	2.720(13)	N(2)–O(6)	1.23(2)
Sn–C(76)	2.113(9)						
Cl(3)–Sn–C(76)	104.9(4)	O(1)–Sn–C(82)	92.6(4)	Sn–O(1)–N(1)	106.0(8)	O(2)–N(1)–O(3)	119(1)
Cl(3)–Sn–C(82)	103.1(4)	O(4)–Sn–Cl(3)	81.5(3)	Sn–O(4)–N(2)	105.1(9)	O(4)–N(2)–O(5)	117(1)
C(76)–Sn–C(82)	151.9(5)	O(4)–Sn–C(76)	91.5(4)	O(1)–N(1)–O(2)	120(1)	O(4)–N(2)–O(6)	112(1)
O(1)–Sn–Cl(3)	81.9(3)	O(4)–Sn–C(82)	91.2(5)	O(1)–N(1)–O(3)	121(1)	O(5)–N(2)–O(6)	131(2)
O(1)–Sn–C(76)	92.8(4)	O(1)–Sn–O(4)	163.4(4)				

(*c*) methanol

C(88)–O(7)	1.52(4)

Table 4. Selected vibrational bands (cm^{-1})

Compound	$\nu_{asym}(NO_3)$	$\nu(NO_3)_{ion}$	$\nu_{sym}(NO_3)$	$\nu(NO_3)$ in-plane	$\delta(NO_3)$ out-of-plane	ν(Sn–C)
$[\{Ag(dppm)(NO_3)\}_2]$	1 410vs	1 370s	1 295s		815m	
$[Ag(dppm)_2][SnPh_2(NO_3)_3]$	1 495s,br		1 280s	1 015m	810m	295m
$[Ag_3Cl_2(dppm)_3][SnPh_2(NO_3)_2Cl]$ *	1 475vs		1 285vs	1 010m	803m	295m
$[Ag(dpam)_2(NO_3)]$		1 340s			830w 815w	
$[Ag(dpam)_2][SnPh_2(NO_3)_3]$	1 490s,br		1 285s	1 010m	830w 807w	295m

* The ν(Sn–Cl) band falls at 270 cm^{-1}.

pentagonal bipyramid with the two phenyl groups occupying the apices, and the C–Sn–C group significantly far from linearity [151.9(5)°]. The equatorial positions are occupied by a chlorine atom and four oxygen atoms from bidentate nitrate groups in a substantially planar arrangement (within 0.02 Å). Both nitrate groups co-ordinate to tin with a short and a long bond as already observed in other seven-co-ordinate nitratodiorganotin derivatives.[2,22,23] This kind of chelation can be classified as bidentate asymmetrical in conformity with the statement of Addison *et al.*[24] that a metal–oxygen bond distance difference of 0.2–0.7 Å for a bidentate nitrate constitutes asymmetrical chelation. The four Sn–O–N angles, ranging from 83.3 to 106.0°, agree with the assertion that the angle at the co-ordinated oxygen atoms is smaller than 110° when the nitrate is bidentate and greater when monodentate. Bond distances and angles at tin agree satisfactorily with the corresponding values reported in a previous *X*-ray structural determination of the same anion.[1]

Although the hydrogen atom from the methanol group has not been directly located in a ΔF map, the occurrence of an O • • • Cl contact of 3.05(2) Å strongly suggests the presence of hydrogen bonding, the hydroxylic O(7) atom being the donor and the Cl(1) atom from the cation at $1 - x$, $1 - y$, $1 - z$ the acceptor. It is worth noting that Cl(2), which is not involved in hydrogen bonding, is bonded closest to Ag. There are no other approaches less than the sum of the corresponding van der Waals radii, the closest intermolecular contact being 3.42(1) Å between O(2) and C(61) at $1 - x$, $1 - y$, $1 - z$. (Extensive use of the Cambridge Crystallographic Database Files has been made for the bibliographic search.)

Infrared Spectra.—Some major bands for the silver and silver–tin complexes along with their possible assignments are given in Table 4. The most important feature in the spectra is the nitrate stretching bands, which appear in the 1 500—1 200 cm^{-1} region.[25,26] In all the three complex salts the separation of the symmetric and asymmetric modes, $\Delta\nu = \nu_{asym}(NO_3) - \nu_{sym}(NO_3)$, is indicative of bidentate behaviour of the nitrate groups towards the tin atom. This assignment is supported by the present *X*-ray diffraction analysis and by our previous spectroscopic findings on nitratotin adducts.[4,27,28]

N.M.R. Spectra.—119-*Tin spectra.* $[Ag_3Cl_2(dppm)_3][SnPh_2(NO_3)_2Cl]\cdot CH_3OH$ is stable in chloroform solution, whereas $[Ag(dppm)_2][SnPh_2(NO_3)_3]$ undergoes rapid decomposition. Nevertheless, in acetone it is sufficiently stable to permit data acquisition at room temperature. The value of the ^{119}Sn chemical shift observed for the anion $[SnPh_2(NO_3)_2Cl]^-$ (-452 p.p.m.) is in good agreement with those observed for other complexes containing seven-co-ordinated tin.[29] The other anion $[SnPh_2(NO_3)_3]^-$, which contains eight-co-ordinate tin in the solid state,[1] exhibits a higher-field resonance (-662 p.p.m.). This is consistent with the general tendency of the tin nucleus to show significantly increasing upfield shifts when the co-ordination number increases from four to five, six, and more.[30]

31-*Phosphorus spectra.* $[Ag_3Cl_2(dppm)_3][SnPh_2(NO_3)_2Cl]\cdot CH_3OH$ contains the unusual trinuclear cation $[Ag_3Cl_2(dppm)_3]^+$, whose ^{31}P n.m.r. spectrum (233—303 K) exhibits an unresolved broad doublet centred at -2.0 p.p.m. [$^1J(Ag^{31}P) = 436$ Hz]. This value, which is significantly higher than those observed in typical four-co-ordinate silver complexes, such as $[Ag(PPh_3)_3I]$[31] and $[Ag(cdppet)_2]^+$,[4] compares well with those found in some silver compounds with distorted trigonal geometry.[32] These complexes[32] exhibit short Ag–P distances and large P–Ag–P angles (compared to those observed in pseudo-tetrahedral compounds) as in the trinuclear cation. Indeed it was pointed out that the Ag–P coupling constants increase with decreasing Ag–P distance and increasing P–Ag–P angle.[33] Fresh acetone solutions of $[Ag(dppm)_2][SnPh_2(NO_3)_3]$, containing the rather unstable $[Ag(dppm)_2]^+$ cation, give at room temperature a broad single peak at 6.2 p.p.m. ($\Delta\nu_{\frac{1}{2}} = 110$ Hz), any information about $^1J(AgP)$ being lost as expected due to the lability of mononuclear silver–phosphine complexes.[34]

Conductivity Data.—On the basis of the conductivity values (Table 1), which agree well with those found for the previously reported silver–tin complexes[4] and similarly approach those of 1 : 1 electrolytes, and taking into account the results of the *X*-ray analysis, it is possible to assign to all compounds an ionic nature. As previously reported for cdppet complexes, and also for the three compounds studied here, the bulky nature of both complex cation and anion justifies the low Λ_M values when compared to those reported in the literature.[35]

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Received 23rd March 1988; *Paper* 8/01183D