SYNTHESIS AND CRYSTAL AND MOLECULAR STRUCTURE OF A SILVER TIN COMPLEX SALT, [Ag(PPh$_3$)$_4$][SnPh$_2$(NO$_3$)$_2$(Cl,NO$_3$)]

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Summary

The crystal and molecular structure of [Ag(PPh$_3$)$_4$][SnPh$_2$(NO$_3$)$_2$(Cl,NO$_3$)] have been determined by X-ray diffraction and refined to a conventional R factor of 0.0732 for 4315 reflections. The structure is composed of discrete [Ag(PPh$_3$)$_4$]$^+$ cations and [SnPh$_2$(NO$_3$)$_2$(Cl, NO$_3$)]$^-$ anions, with the latter showing a disordered distribution involving Cl$^-$ and one NO$_3$$^-$ group, each with an occupancy of 0.5. The Ag atom is bonded to four triphenylphosphine molecules in a slightly distorted tetrahedral environment. Taken account of the disorder, the coordination about tin can be described as distorted pentagonal or hexagonal bipyramidal with the equatorial positions occupied by the disordered ligand and two NO$_3$ groups, the phenyl rings being at the apices.

Introduction

During our studies of the coordination chemistry of organotin adducts, we have recently investigated the synthesis and structural characterization of compounds containing both silver and tin [1]. Only a few examples of these derivatives have appeared in the literature [2,3] but there is interest in the field of photography [4].

We describe below the synthesis and X-ray crystal structure study of a new silver tin complex salt of the formula [Ag(PPh$_3$)$_4$][SnPh$_2$(NO$_3$)$_2$(Cl,NO$_3$)].

Experimental

Preparation

SnPh$_2$(NO$_3$)$_2$, prepared as previously described [1], was treated with a 4 molar equivalent of Ph$_3$P in acetone. The solution was warmed to 50–60°C and stirred for 1 h then set aside. After some days, a white crystalline product of the formula [Ag(PPh$_3$)$_4$][SnPh$_2$(NO$_3$)$_2$(Cl,NO$_3$)] was isolated (Found: C, 63.06; H, 4.62; N, 2.09; C$_{84}$H$_{70}$AgCl$_{0.5}$N$_{2.5}$O$_{7.5}$P$_4$Sn calcd.: C, 62.95; H, 4.40; N, 2.18%). AgNO$_3$ and

TABLE 1

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$)

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Sn	2078(1)	5827(1)	8983(1)	C(34)	36(9)	3784(13)	7816(13)
Ag	2559(1)	324(1)	3744(1)	C(35)	336(9)	4355(14)	7216(14)
P(1)	2166(2)	−1083(3)	4574(3)	C(36)	825(9)	3903(13)	6149(13)
P(2)	1452(2)	2362(3)	4330(3)	C(37)	3387(8)	580(12)	998(12)
P(3)	3053(2)	−289(3)	1710(3)	C(38)	3041(9)	1648(14)	1448(13)
P(4)	3536(2)	307(3)	4369(3)	C(39)	3238(10)	2391(15)	912(15)
Cl	851(5)	7489(8)	9734(7)	C(40)	3809(10)	2010(15)	−66(14)
O(1)	1937(9)	5642(13)	7427(12)	C(41)	4119(11)	955(17)	−526(15)
O(2)	2845(8)	4362(12)	7396(11)	C(42)	3938(10)	225(15)	21(15)
O(3)	2567(16)	4299(24)	6120(25)	C(43)	2453(8)	−323(11)	1143(11)
O(4)	3096(9)	4731(13)	9564(13)	C(44)	2139(9)	−1026(13)	1431(13)
O(5)	2195(7)	6175(10)	10539(9)	C(45)	1639(10)	−1083(15)	1055(14)
O(6)	3056(13)	5604(19)	10931(20)	C(46)	1451(11)	−345(17)	406(15)
O(7)	1093(16)	6974(24)	8759(24)	C(47)	1692(10)	347(15)	152(14)
O(8)	1071(16)	7357(24)	10268(23)	C(48)	2222(9)	398(13)	485(13)
O(9)	143(19)	8093(29)	9807(27)	C(49)	3813(8)	−1623(12)	1157(11)
N(1)	2404(14)	4833(21)	7034(20)	C(50)	3900(10)	−2238(15)	271(14)
N(2)	2813(10)	5410(15)	10302(15)	C(51)	4512(12)	−3254(18)	−118(17)
N(3)	769(17)	7475(26)	9604(25)	C(52)	5007(11)	−3650(17)	327(16)
C(1)	1677(8)	−758(11)	6002(11)	C(53)	4917(12)	3023(17)	1191(17)
C(2)	1235(8)	−1206(12)	6485(12)	C(54)	4276(9)	−1963(14)	1625(13)
C(3)	831(9)	−870(13)	7563(13)	C(55)	3263(8)	733(12)	5735(11)
C(4)	870(10)	−107(15)	8118(15)	C(56)	2617(9)	1682(14)	6233(13)
C(5)	1351(11)	311(16)	7628(15)	C(57)	2385(11)	2092(17)	7292(16)
C(6)	1760(9)	−24(14)	6547(13)	C(58)	2790(11)	1536(16)	7828(16)
C(7)	1494(7)	−1105(11)	4133(10)	C(59)	3410(11)	602(16)	7383(15)
C(8)	1448(8)	−2027(12)	3918(12)	C(60)	3660(9)	181(14)	6314(13)
C(9)	907(9)	−1957(14)	3541(13)	C(61)	4298(8)	−1046(12)	4095(12)
C(10)	425(8)	−973(13)	3452(12)	C(62)	4095(9)	−1801(14)	4484(13)
C(11)	470(8)	−75(13)	3704(12)	C(63)	4674(12)	−2899(17)	4280(16)
C(12)	1013(8)	−117(12)	4038(12)	C(64)	5385(11)	−3113(16)	3734(15)
C(13)	2807(8)	−2490(12)	4328(11)	C(65)	5555(10)	−2334(16)	3370(15)
C(14)	2887(9)	−3048(14)	5101(13)	C(66)	4993(9)	−1258(13)	3538(12)
C(15)	3413(11)	−4179(16)	4804(16)	C(67)	3996(7)	1085(11)	3764(11)
C(16)	3787(11)	−4672(17)	3803(17)	C(68)	4144(9)	1098(13)	2705(13)
C(17)	3715(11)	−4111(16)	3018(15)	C(69)	4498(9)	1678(14)	2224(14)
C(18)	3194(9)	−2995(14)	3293(13)	C(70)	4691(9)	2241(13)	2748(13)
C(19)	1726(7)	3377(11)	3856(10)	C(71)	4543(10)	2246(15)	3794(14)
C(20)	1373(8)	4154(12)	3349(11)	C(72)	4168(9)	1686(13)	4322(12)
C(21)	1622(9)	4893(13)	3004(13)	C(73)	2791(9)	6475(13)	8253(12)
C(22)	2200(9)	4903(13)	3146(13)	C(74)	2480(11)	7549(17)	8197(16)
C(23)	2535(9)	4149(13)	3662(12)	C(75)	2953(12)	8018(18)	7713(17)
C(24)	2324(8)	3372(12)	3989(11)	C(76)	3686(12)	7383(18)	7329(16)
C(25)	722(7)	2618(11)	3896(11)	C(77)	3960(12)	6323(18)	7406(16)
C(26)	13(8)	3299(12)	4520(12)	C(78)	3520(11)	5841(16)	7908(16)
C(27)	−538(9)	3472(13)	4146(13)	C(79)	1644(8)	4804(13)	9529(12)
C(28)	−355(9)	2965(13)	3152(13)	C(80)	1161(10)	4717(14)	9197(13)
C(29)	348(9)	2295(13)	2540(12)	C(81)	858(11)	4029(16)	9565(16)
C(30)	898(8)	2104(12)	2909(12)	C(82)	1042(10)	3413(15)	10300(14)
C(31)	943(7)	2921(11)	5725(10)	C(83)	1506(11)	3528(16)	10665(15)
C(32)	661(9)	2334(13)	6310(12)	C(84)	1812(9)	4200(14)	10285(13)
C(33)	209(9)	2746(14)	7373(13)				

SnPh$_2$Cl$_2$ used as reagents in the preparation of SnPh$_2$(NO$_3$)$_2$ are undoubtedly responsible for the presence of silver and chlorine. Treatment of pure SnPh$_2$(NO$_3$)$_2$ with PPh$_3$ and AgCl (1/4/1 molar ratio) in acetone gave a microcrystalline product with an infrared spectrum identical with that of the title compound.

Single crystals suitable for X-ray analysis were obtained as colourless tablets by recrystallization from acetone.

Collection and reduction of X-ray data

Crystal data: C$_{84}$H$_{70}$AgCl$_{0.5}$N$_{2.5}$O$_{7.5}$P$_4$Sn, *M* 1602.59, triclinic, space group $P\bar{1}$, *a* 22.43(2), *b* 14.13(1), *c* 13.96(1) Å, α 90.59(5), β 69.82(4), γ 64.58(6)°, *U* 3685(5) Å^3, *Z* = 2, *D*$_c$ 1.444 g cm^{-3}, *F*(000) 1634, μ(Mo-*K$_\alpha$*) 6.8 cm^{-1}.

The unit-cell parameters were determined by a least-squares refinement of 2θ values for 16 reflections automatically centred. 10353 unique reflections having 5.0 < 2θ < 48.0° were measured on a Siemens AED single-crystal diffractometer in conventional θ/2θ scan method, with Nb-filtered Mo-*K$_\alpha$* radiation ($\bar{\lambda}$ 0.71069 Å). A total of 4315 reflections with *I* > 3σ(*I*) based on counting statistics were regarded as observed and employed in subsequent calculations. Electronic and crystal stability was monitored by periodic measurement of a standard reflection, and no significant variations were noted during the time required to collect the data. Intensities were reduced to structure amplitudes by applying the usual Lorentz-polarization factor. Absorption corrections were omitted in view of the low linear absorption coefficient.

Solution and refinement of the structure

The structure was solved using the heavy-atom technique. Both Ag and Sn atoms were located from a three-dimensional Patterson map. The remaining non-hydrogen atoms were located from subsequent sequences of Fourier and difference Fourier syntheses, whose phases were calculated using only the Ag and Sn atoms. Refinement was by full-matrix least-squares. Anisotropic thermal parameters were assigned only to the Ag, Sn, and P atoms, the remaining atoms being refined isotropically. No

TABLE 2

SELECTED BOND DISTANCES (Å) AND ANGLES (deg.)

In the [Ag(PPh$_3$)$_4$]$^+$ cation

		P(1)–C(1)	1.85(1)	P(3)–C(37)	1.83(2)
Ag–P(1)	2.631(5)	P(1)–C(7)	1.83(2)	P(3)–C(43)	1.80(2)
Ag–P(2)	2.746(5)	P(1)–C(13)	1.82(1)	P(3)–C(49)	1.83(1)
Ag–P(3)	2.645(5)	P(2)–C(19)	1.84(2)	P(4)–C(55)	1.80(2)
Ag–P(4)	2.615(6)	P(2)–C(25)	1.83(2)	P(4)–C(61)	1.86(1)
		P(2)–C(31)	1.84(1)	P(4)–C(67)	1.84(2)
P(1)–Ag–P(2)	113.0(2)	P(1)–Ag–P(4)	107.8(2)	P(2)–Ag–P(4)	108.0(2)
P(1)–Ag–P(3)	105.9(2)	P(2)–Ag–P(3)	109.6(2)	P(3)–Ag–P(4)	112.6(2)

In the [SnPh$_2$(NO$_3$)$_2$(Cl,NO$_3$)]$^-$ anion

Sn–C(73)	2.14(2)	Sn–O(2)	2.52(1)	Sn–Cl	2.569(9)
Sn–C(79)	2.08(2)	Sn–O(4)	2.56(2)	Sn–O(7)	2.24(3)
Sn–O(1)	2.33(2)	Sn–O(5)	2.35(2)	Sn–O(8)	2.43(2)
C(73)–Sn–C(79)	164.2(7)	O(4)–Sn–O(5)	51.7(5)	O(5)–Sn–O(8)	63.5(8)
O(1)–Sn–O(2)	49.7(6)	O(5)–Sn–Cl	86.5(4)	O(8)–Sn–O(7)	54.5(11)
O(2)–Sn–O(4)	82.1(6)	Cl–Sn–O(1)	90.3(6)	O(7)–Sn–O(1)	58.7(10)

hydrogen atoms were discernible in ΔF maps. In view of the large number of variable parameters (443), block matrices were used during the last cycles of refinement. The final discrepancy index R was 0.0732 based on 4315 contributing reflections. The highest residual electron density was 1.1 e Å^{-3}, near the silver atom. Complex neutral-atom scattering factors were employed, with the weighting $w = [\sigma^2(F_0) + 0.0026\,F_0^2]^{-1}$ for the final stages of refinement. The scattering for Ag, Sn, P and Cl was corrected for the real and imaginary components of anomalous dispersion [5]. Calculations were carried out with SHELX 76 [6] and local programs on the Cyber 76 computer of CINECA (Casalecchio, Bologna) with financial support from the University of Parma.

The final atomic coordinates are given in Table 1 and the relevant bond distances and angles in Table 2. Lists of thermal parameters and structure factors are available upon request from the authors.

Results and discussion

The crystal structure of the title compound consists of discrete [Ag(PPh$_3$)$_4$]$^+$ cations and [SnPh$_2$(NO$_3$)$_2$(Cl,NO$_3$)]$^-$ anions, with the geometries illustrated in
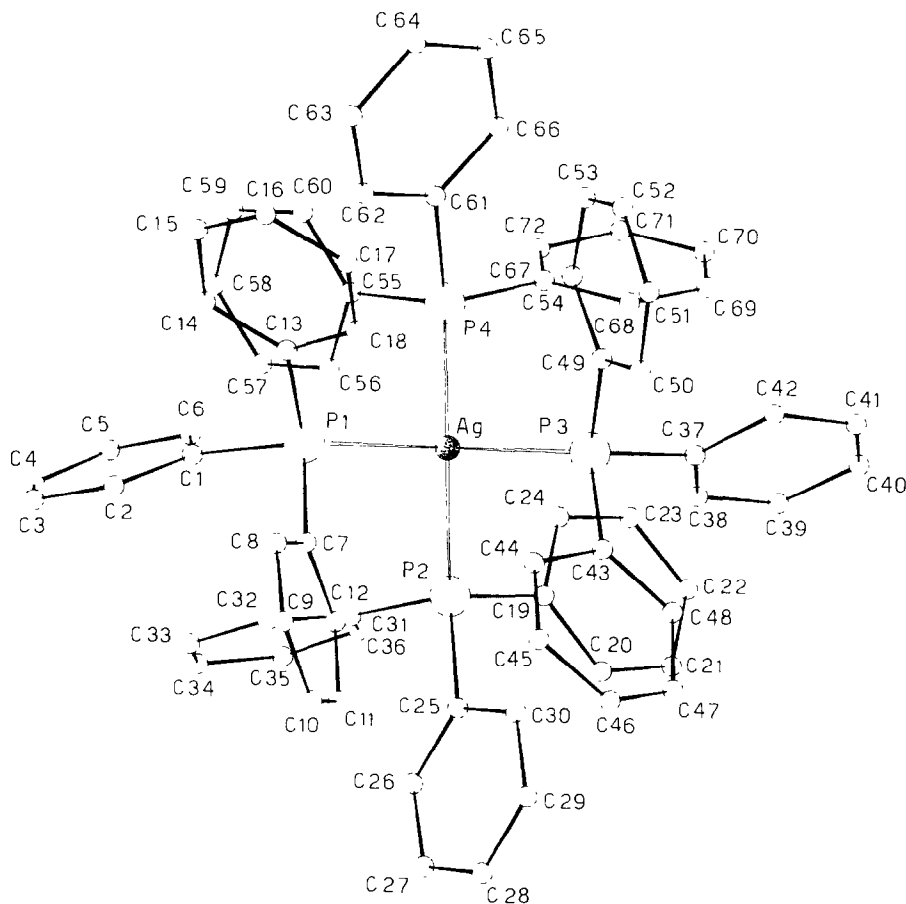

Fig. 1. Perspective view of the [Ag(PPh$_3$)$_4$]$^+$ ion with atomic labels.

Figs. 1 and 2, respectively. Of major interest in the context of this structural study is the joint presence of silver and tin. The structure of the complex salt, as a whole, shows a striking similarity with those observed in the two closely related triphenyl-arsine derivatives recently examined by X-ray diffraction, namely $[Ag(AsPh_3)_4]$-$[SnPh_2(NO_3)_3]$ and $[Ag(AsPh_3)_4][SnPh_2(NO_3)_2Cl]$ [1], both of which are isostructural with the present compound.

In the complex cation the four triphenylphosphine molecules are bonded with rather long P–Ag distances (from 2.615(6) to 2.746(5) Å) to the silver atom, to give a slightly distorted tetrahedral coordination about the metal, with the angles at Ag varying from 105.9(2) to 113.0(2)°.

It is known that in metal complexes of PPh_3 and $AsPh_3$, since the covalent radius of P is less than that of As, the M–P bonds are usually shorter than corresponding M–As bonds in similar conditions, such as the nature of M, the number, n, of PPh_3 or $AsPh_3$, and the coordination geometry; the following examples illustrate this:

$n = 1$

Au^I–P 2.235(3) Å in $Au(PPh_3)Cl$ [7], Au^I–As 2.342 (5) Å in $Au(AsPh_3)Br$ [8];
Ag^I–P 2.369(6) Å in $Ag(PPh_3)NO_3$ [9], Ag^I–As 2.471(2) Å in $Ag(AsPh_3)NO_3$ [1];
Cu^I–P 2.242(4) Å in $[Cu(PPh_3)I]_4$ [10], Cu^I–As from 2.366(3) to 2.384(3) Å in $[Cu(AsPh_3)I]_4 \cdot C_6H_6$ [11]

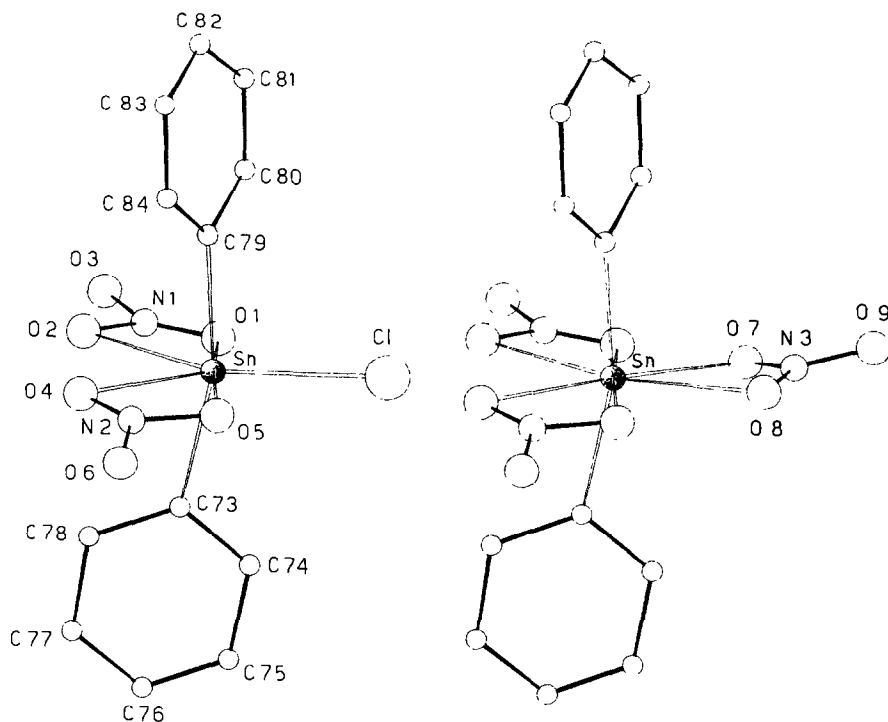

Fig. 2. Perspective view of the $[SnPh_2(NO_3)_2(Cl,NO_3)]^-$ ion with atomic labels, showing the disordered distribution involving Cl^- and one NO_3 group.

$n = 2$

Pt^0–P 2.264(1), 2.271(1) Å in Pt(cyclohexyne)(PPh$_3$)$_2$ and 2.264(1), 2.270(1) Å in Pt(cycloheptyne)(PPh$_3$)$_2$ [12], Pt^0–As 2.435(1), 2.436(1) Å in Pt(C$_2$F$_4$)(AsPh$_3$)$_2$ [13];
Ag^I–P 2.467(2), 2.472(2) Å in Ag(PPh$_3$)$_2$Cl [14], Ag^I–As 2.535(2), 2.521(3) Å in Ag(AsPh$_3$)$_2$NO$_3$ [1]

$n = 3$

Ag^I–P 2.552(1), 2.556(1), 2.520(1) Å in Ag(PPh$_3$)$_3$Cl [15], Ag^I–As 2.608(3), 2.617(2), 2.678(2) Å in Ag(AsPh$_3$)$_3$NO$_3$ [1].

In view of this, we were surprised to find the Ag–P distances in the cation in the present study to be essentially identical to the Ag–As distances in the two above-mentioned structures containing [Ag(AsPh$_3$)$_4$]$^+$ cations (range: 2.643(4)–2.700(5) Å and 2.657(3)–2.698(3) Å, respectively) [1]. The high number of PPh$_3$ molecules bonded to Ag is undoubtedly a decisive factor for such a behaviour. In fact the bulk of four PPh$_3$ groups must be closely comparable to that of four AsPh$_3$ groups, and so closer approach of the former ligands to the metal is prevented and the silver environment is not significantly perturbed by the replacement of As by P. Unfortunately, there is no further evidence to support this assertion, since we are unaware of any other metal compounds containing four AsPh$_3$ in the coordination sphere. As regards the Ag–P distances found here, which, to our knowledge, are the longest such distance ever observed, the only compound having four P donors with which comparison can be made is tetrakis(4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane) silver perchlorate [16], but no structural information (coordinates or bond distances) is given in the paper as revealed by a search using the Cambridge Crystallographic Data Files.

The P atoms are tetrahedrally surrounded by one Ag and three C atoms. The PPh$_3$ ligand geometry shows no unusual features; the P–C bond distances are within the normal range for such bonds, the mean P–C distance found in our compound being 1.83(2) Å and the Ag–P–C angles are all close to or greater than 109.5°, while the C–P–C angles are all below the tetrahedral value. Within each Ph$_3$P group all three phenyl rings are planar and P is slightly out (0.01–0.20 Å) of the plane of each phenyl group.

In the anion the stereochemistry in the coordination sphere of tin approaches pentagonal or hexagonal bipyramidal geometry, as judged by the presence in the equatorial plane, in addition to two bidentate nitrate groups, of a chloride ion or a third bidentate nitrate, these two ligands being statistically interchangeable with a 50% occupancy factor. In each of the three NO$_3$ ligands the two O–Sn bonds differ by ca. 0.20 Å, so that these groups may be considered as asymmetrically bidentate ligands. The two phenyl rings occupy the axial positions of the bipyramid at an angle of 164.2(7)°. The sum of the angles subtended at the tin atom in the equatorial plane is 360.3°.

There are no unusually short interionic contacts, so it seems that the complex ions are held together in the crystal by Van der Waals interactions only. The closest anion-cation approaches are 3.27(2) Å between O(2) and C(65) at $1 - x, \bar{y}, 1 - z$ and 3.32(5) Å between O(8) and C(45) at $x, 1 + y, 1 + z$.

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