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Synthesis and Structural Studies on Silver–Tin Complex Salts with *cis*-1,2-Bis(diphenylphosphino)ethylene*

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Abstract

Three new silver–tin complex salts with *cis*-1,2-bis(diphenylphosphino)ethylene have been synthesized. IR, ^{31}P and ^{119}Sn NMR and conductivity data are reported and discussed together with the X-ray crystal structure of one of them, $[Ag(cdppet)_2][SnPh_3(NO_3)_2]$. The silver atom is distorted tetrahedrally surrounded by the four phosphorus atoms of the two cdppet ligands. The tin atom is in a slightly distorted trigonal bipyramidal geometry with the phenyl carbon atoms in the equatorial plane and two oxygen atoms from monodentate nitrate groups at the apices.

Introduction

As part of our continuing interest into the structural chemistry of organotin adducts with P or As containing ligands [1–3], and in order to produce new compounds containing two different metal atoms, we have synthesized a series of silver–tin complexes with phosphine or arsine ligands [4–6].

The coexistence in the same compound of tin and silver increases the interest in the chemical and structural properties of these derivatives, the interest being mainly due to the poor appearance in the literature of such compounds [7–9] and to their ionic nature.

In this paper we describe the synthesis of new silver–tin complex salts with *cis*-1,2-bis(diphenylphosphino)ethylene (cdppet) together with some important features of their IR and ^{31}P and ^{119}Sn NMR spectra. The crystal and molecular structure of $[Ag(cdppet)_2][SnPh_3(NO_3)_2]$ is also reported.

Experimental

Reagents

Solvents were dried and distilled before use. $SnPh_3Cl$, $SnPh_2Cl_2$, $AgNO_3$, and *cis*-1,2-bis(diphenylphosphino)ethylene (cdppet) were commercially available and were used without further purification.

The preparation of $SnPh_3NO_3$ and $SnPh_2(NO_3)_2$ was reported previously [10, 11]. A further purification on $SnPh_2(NO_3)_2$ under nitrogen atmosphere from an acetonitrile/acetone (1:5 *v*/*v*) mixture was carried out. The purified product was then stored under nitrogen atmosphere at 0 °C.

$Ag(cdppet)_2NO_3$

Silver nitrate and cdppet (1:2 molar ratio) were dissolved in a methanol/tetrahydrofuran (3:1 *v*/*v*) mixture and allowed to stir at room temperature for 1 h. After several hours by slow evaporation of the solvents, a white crystalline product was isolated. The crude product was recrystallized from methanol. Analytical data, which are reported in Table I for all compounds together with conductivity data, agree with the formula $Ag(cdppet)_2NO_3$.

Preparation of Silver–Tin Complex Salts

$[Ag(cdppet)_2][SnPh_2(NO_3)_3]$ and $[Ag(cdppet)_2][SnPh_3(NO_3)_2]$ were prepared as follows. Diphenyl or triphenyltin nitrate, silver nitrate and cdppet (1:1:2 molar ratios) were dissolved in an acetone/acetonitrile (7:1 *v*/*v*) mixture and allowed to stir at room temperature, under nitrogen atmosphere, for 2 h. After several hours by slow evaporation of the solvents, white and pale yellow crystals of the diphenyl and triphenyltin adducts, respectively, were obtained in high yields (~80%). The compounds are air stable and slightly photosensitive. Analytical data agree with the formulae $[Ag(cdppet)_2][SnPh_2(NO_3)_3]$ and $[Ag(cdppet)_2][SnPh_3(NO_3)_2]$. Both compounds can also be obtained from the reaction of organotin nitrate with the preformed complex $Ag(cdppet)_2NO_3$ in acetonitrile/chloroform solution.

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TABLE I. Analytical[a] and Conductivity Data

	C (%)	H (%)	N (%)	Sn (%)	Ag (%)	Λ_M (10^{-3} M)[b] (ohm^{-1} cm^2 mol^{-1})
$Ag(cdppet)_2NO_3$	65.02 (64.88)	4.73 (4.61)	1.53 (1.46)		11.88 (11.21)	
$[Ag(cdppet)_2][SnPh_2(NO_3)_3]$	56.64 (56.54)	4.06 (4.00)	2.99 (3.09)	8.04 (8.73)	9.14 (7.93)	12.5
$[Ag(cdppet)_2][SnPh_3(NO_3)_2]$	60.11 (61.16)	4.28 (4.33)	2.13 (2.04)	8.19 (8.63)	8.17 (7.85)	15.0
$[Ag(cdppet)_2][SnPh_2(NO_3)Cl_2]$	59.01 (58.83)	4.44 (4.17)	1.31 (1.07)	8.40 (9.08)	8.90 (8.26)	10.8

[a] Calculated values in parentheses. [b] Λ_M (10^{-3} M) of $[Ag(Ph_3As)_4][SnPh_2(NO_3)_3]$ (ref. 4) in nitrobenzene = 12.5 ohm^{-1} cm^2 mol^{-1}.

$[Ag(cdppet)_2][SnPh_2(NO_3)Cl_2]$

$SnPh_2Cl_2$ dissolved in acetonitrile was added to a chloroform solution of $Ag(cdppet)_2NO_3$ (1:1 molar ratio) and allowed to stir at room temperature under inert atmosphere for 1 h. No precipitation of silver chloride was observed. The solution was then concentrated to dryness *in vacuo* and the crude product was recrystallized from a chloroform/hexane mixture. Analytical data agree with the formula $[Ag(cdppet)_2][SnPh_2(NO_3)Cl_2]$.

Procedure for the Determination of Silver and Tin

Considerable difficulty was encountered in the quantitative analysis of silver and tin, owing to the presence in the same product, besides these elements, of phosphorus, chloride or nitrate anion and organic moieties.

Attempts to decompose and dissolve the silver–tin complexes in aqueous solution by means of concentrated hydrochloric, nitric and sulphuric acids failed. The proposed method was applied satisfactorily to the determination of silver and tin in several samples. To 0.05 g of solid sample in a calibrated flask were added about 6 cm^3 of concentrated sulphuric acid. The suspension was heated until white vapours were observed, and then an aqueous 1.0% (*m*/*v*) solution of oxalic acid was added.

Working standard solutions were prepared in a similar way by weighting $SnPh_2(NO_3)_2$ (or $SnPh_3NO_3$), $AgNO_3$ and cdppet in suitable molar ratios.

Measurements

Elemental C, H, and N analyses were made on a Perkin-Elmer 240 automatic equipment. Determination for silver and tin was by atomic absorption spectroscopy on a Perkin-Elmer 303-HGA 70 instrument (λ = 328 nm for silver and 226 nm for tin).

The IR spectra were recorded as KBr discs using a Perkin-Elmer 283 B spectrophotometer in the 4000–200 cm^{-1} region.

^{119}Sn and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker CXP 200 at 74.5 and 81 MHz respectively using ^2H lock. Chloroform-d was used as a solvent. Chemical shifts are given relative to external $SnMe_4$ and 85% H_3PO_4. A positive sign indicates a shift to low field of the resonance.

Conductivity measurements were made on a Philips PW 9504/00 conductivity bridge in nitrobenzene (10^{-3} M at 25 °C).

Crystallography of $[Ag(cdppet)_2][SnPh_3(NO_3)_2]$

Data collection and processing of X-ray diffraction data

All X-ray measurements were carried out with a Siemens AED three-circle diffractometer on line to a General Automation Jumbo 220 minicomputer by using Mo Kα radiation. A crystal of approximate dimensions 0.28 × 0.31 × 0.50 mm was mounted on the diffractometer and a triclinic symmetry was identified via a quick search for intense, low-order reflections. A cell reduction failed to show the presence of a higher symmetry cell and the choice of space group $P\bar{1}$ was justified by intensity distribution statistics and successful refinement of the structure. The unit-cell dimensions, which were obtained from least-squares refinement of the angular settings of a number of accurately centred reflections widely distributed throughout the reciprocal space, are presented in Table II, together with details of data collection. One hemisphere of data was collected at room temperature and the reflection profiles were analyzed according to a modified version of the Lehmann and Larsen procedure [12]. The 7426 unique reflections obeying the condition $I > 2\sigma(I)$ had been retained out of a total of 12 145 measured reflections. One control reflection indicated that, by completion of the data collection, no decomposition had occurred. The intensity data were corrected for Lorentz and polarization effects. Corrections for

TABLE II. Crystallographic Data and Intensity Collection Details

Formula	$C_{70}H_{59}AgN_2O_6P_4Sn$
Molecular weight	1374.70
Space group	$P\bar{1}$
a (Å)	17.475(8)
b (Å)	10.327(5)
c (Å)	17.758(7)
α (°)	95.00(3)
β (°)	77.43(2)
γ (°)	88.75(3)
V (Å^3)	3113(2)
Z	2
D_m (g cm^{-3})	1.485
D_x (g cm^{-3})	1.466
Radiation, λ (Å)	Mo Kα, 0.71069
$F(000)$	1396
μ(Mo Kα) (cm^{-1})	8.67
Scan method	θ–2θ
Takeoff angle (°)	4
2θ range (°)	6.0–52.0
Data collection range	$\pm h \pm k + l$
No. reflections measured	12145
No. observed reflections	7426
Absorption correction (min–max)	0.9027–1.0715
Extinction correction (min-max)	0.9322–1.0427

absorption and extinction were also applied after isotropic refinement, using the empirical method of Walker and Stuart [13].

Structure solution and refinement

The positional parameters of the silver atom were derived from a three-dimensional Patterson map and were subsequently used as an initial phasing model for a Fourier synthesis, which revealed the positions of the tin and the four phosphorus atoms. All other non-hydrogen atoms were located through the usual combination of structure factor and difference Fourier synthesis calculations. The structure was refined by using a full-matrix least-squares procedure based on F, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$. It was possible to locate two alternative positions for one of the two NO_3^- groups which was found to exhibit disorder. The best resolution of this ion has two oxygen atoms on a well-defined site of unit occupancy, and nitrogen and the third oxygen, O(6), disordered over two sites with a 0.60/0.40 occupancy ratio. All atoms were allowed anisotropic vibration except those of the disordered NO_3^- ion, which were refined isotropically. The hydrogen atoms from the phenyl rings were placed in calculated positions and included in the structure factor calculations, while the ethylenic hydrogens were ignored. Due to the large number of reafinable parameters, all the phenyl rings were refined as rigid bodies and during the final cycles of refinement cation and anion were alternately allowed to vary. The final residual indices for 624 variables refined against 7426 data were $R = 0.0450$, $R_w = 0.0548$, $GOF = 0.7861$ with weights $w = 0.7258/[\sigma^2(F_o) + 0.001562F_o^2]$. The final difference Fourier map contained two residual peaks of about 0.8 e Å^{-3} in the vicinity of the disordered NO_3^- group, possibly indicating a not completely adequate resolution of the atoms, but was devoid of any significant features elsewhere. During all calculations the analytical scattering factors for neutral atoms were corrected for both $\Delta f'$ and $\Delta f''$ terms [14].

The calculations were performed on CDC Cyber 76 and GOULD 32/77 computers, using the programs of the SHELX-76 package [15]. The other programs used in the structure determination have been cited elsewhere [16].

The final atomic coordinates for non-hydrogen atoms are listed in Table III, and relevant bond distances and angles are given in Table IV. See also "Supplementary Material".

Results and Discussion

Important factors governing the formation of silver–tin complex salts seem to be the nature and the size of the diphosphine ligand. The particular geometry of the cdppet molecule forces a bidentate chelating behaviour towards the silver atom, favouring in this way the formation of $[Ag(cdppet)_2]^+$ cations. Attempts to isolate similar complexes with different diphosphines containing the P–C–C–P moiety, such as 1,2-bis(diphenylphosphino)ethane and *trans*-1,2-bis(diphenylphosphino)ethylene, were in fact unsuccessful; in these cases only monometallic adducts of tin and silver with the P-ligand were obtained.

The formation of these complex salts is also favoured by the tendency of the tin atom to produce stereochemistries of high coordination number also in the form of a complex anion.

X-ray Structure of $[Ag(cdppet)_2][SnPh_3(NO_3)_2]$

The crystal structure consists of discrete well separated cations $[Ag(cdppet)_2]^+$ and anions $[SnPh_3(NO_3)_2]^-$. ORTEP diagrams and atom labelling schemes for the two ions are in Figs. 1 and 2, with thermal ellipsoids enclosing 50% of the electron probability distribution.

The coordination polyhedron around the silver atom is a deformed tetrahedron and involves four phosphorus atoms from two cdppet ligands. As can be seen in Table IV, there is appreciable distortion from the ideal tetrahedral geometry as a result of constraints imposed by the cdppet ligand structure, the angles at silver ranging from 83.9(1)° to 127.8(1)°. The Ag–P bond distances are virtually identical, as they fall in the very narrow range of 2.463–2.479 Å The only other example of a structurally charac-

TABLE III. Fractional Atomic Coordinates (× 10^5 for Ag and Sn, and × 10^4 for P, O, N, and C)[a]

Atom	*x/a*	*y/b*	*z/c*
Ag	26644(2)	4885(4)	22615(2)
Sn	25517(2)	44990(4)	72842(2)
P(1)	3881(1)	1704(1)	1984(1)
P(2)	2074(1)	2384(1)	1800(1)
P(3)	2047(1)	−146(1)	3563(1)
P(4)	2478(1)	−1794(1)	1834(1)
C(1)	4141(2)	2589(4)	2813(2)
C(2)	3755(2)	3770(4)	3138(2)
C(3)	3915(2)	4381(4)	3816(2)
C(4)	4460(2)	3811(4)	4169(2)
C(5)	4846(2)	2630(4)	3844(2)
C(6)	4686(2)	2019(4)	3166(2)
C(7)	4817(2)	1073(4)	1407(2)
C(8)	5465(2)	1854(4)	1271(2)
C(9)	6187(2)	1330(4)	842(2)
C(10)	6261(2)	24(4)	548(2)
C(11)	5613(2)	−757(4)	684(2)
C(12)	4891(2)	−233(4)	1114(2)
C(13)	3639(3)	3015(6)	1446(3)
C(14)	2908(3)	3304(5)	1374(4)
C(15)	1525(2)	2164(4)	1048(2)
C(16)	1845(2)	2369(4)	279(2)
C(17)	1419(2)	2084(4)	−289(2)
C(18)	672(2)	1592(4)	−88(2)
C(19)	352(2)	1387(4)	682(2)
C(20)	778(2)	1673(4)	1250(2)
C(21)	1480(2)	3543(3)	2544(2)
C(22)	812(2)	4207(3)	2441(2)
C(23)	339(2)	4972(3)	3061(2)
C(24)	533(2)	5075(3)	3784(2)
C(25)	1202(2)	4411(3)	3888(2)
C(26)	1675(2)	3646(3)	3267(2)
C(27)	1111(2)	672(4)	4024(2)
C(28)	599(2)	924(4)	3546(2)
C(29)	−107(2)	1628(4)	3853(2)
C(30)	−300(2)	2082(4)	4637(2)
C(31)	213(3)	1830(4)	5114(2)
C(32)	918(2)	1125(4)	4808(2)
C(33)	2565(2)	−203(4)	4326(2)
C(34)	2607(2)	−1281(4)	4740(2)
C(35)	3006(2)	−1218(4)	5341(2)
C(36)	3363(2)	−76(4)	5530(2)
C(37)	3321(2)	1002(4)	5117(2)
C(38)	2922(2)	939(4)	4515(2)
C(39)	1759(3)	−1811(5)	3378(3)
C(40)	1921(3)	−2459(5)	2682(3)
C(41)	1995(2)	−2318(3)	1065(2)
C(42)	1804(2)	−3607(3)	922(2)
C(43)	1513(2)	−3987(3)	269(2)
C(44)	1411(2)	−3077(3)	−241(2)
C(45)	1602(2)	−1788(3)	−98(2)
C(46)	1893(2)	−1408(3)	555(2)
C(47)	3367(2)	−2815(3)	1595(2)
C(48)	3759(2)	−3090(3)	2172(2)
C(49)	4503(2)	−3704(3)	1971(2)
C(50)	4856(2)	−4045(3)	1193(2)
C(51)	4464(2)	−3770(3)	616(2)
C(52)	3719(2)	−3156(3)	817(2)
C(53)	2369(2)	6548(3)	7460(2)
C(54)	1608(2)	7073(3)	7552(2)
C(55)	1468(2)	8418(3)	7667(2)
C(56)	2088(2)	9238(3)	7691(2)
C(57)	2848(2)	8713(3)	7599(2)
C(58)	2989(2)	7367(3)	7484(2)
C(59)	1533(2)	3372(4)	7466(2)
C(60)	1468(2)	2370(4)	6907(2)
C(61)	809(2)	1613(4)	7013(2)
C(62)	213(2)	1859(4)	7679(2)
C(63)	277(2)	2862(4)	8238(2)
C(64)	937(2)	3618(4)	8132(2)
C(65)	3615(2)	3349(4)	6961(2)
C(66)	3691(2)	2300(4)	7388(2)
C(67)	4357(2)	1467(4)	7177(2)
C(68)	4948(2)	1683(4)	6538(2)
C(69)	4872(2)	2732(4)	6111(2)
C(70)	4206(2)	3565(4)	6322(2)
O(1)	2505(2)	4256(4)	8555(2)
O(2)	3532(3)	5405(5)	8457(3)
O(3)	3156(3)	4382(6)	9456(3)
N(1)	3084(3)	4697(5)	8830(3)
O(4)	2487(4)	4494(6)	6038(4)
O(5)	2309(4)	5615(6)	5152(4)
O(6)	3267(5)	5767(9)	5735(5)
O(6)′	1510(9)	5327(13)	6113(8)
N(2)	2670(7)	5367(11)	5656(7)
N(2)′	2088(10)	5113(14)	5767(9)

[a] e.s.d.s given in parentheses.

terized silver(I) compound having four P donors, of which we are aware, is the $[Ag(PPh_3)_4]^+$ cation. Three X-ray crystal analyses are reported in the literature for this ion in its salts of formula $[Ag(PPh_3)_4]X$. The reports, with the relative Ag–P bond distances, are as follows: X = $[SnPh_2(NO_3)_2(Cl, NO_3)]$, 2.631(5), 2.746(5), 2.645(5), 2.615(6) Å [5]; X = ClO_4, 2.650(2), 2.668(2) Å [17]; X = NO_3, 2.643(3), 2.671(4) Å [18]. Compared with those in the present compound, the above Ag–P bonds are considerably longer, presumably as a consequence of the steric bulk of the four phosphine groups which prevent a closer approach of the ligands to the silver atom. The values found here, however, agree very satisfactorily with those reported for tetrahedral silver(I) derivatives having in the coordination sphere not more than two P donors. A number of such examples is available at this time, as shown by a search in the Cambridge Crystallographic Data File. Some typical values are: 2.455(3) and 2.503(5) Å in $[Ag(PPh_3)_2(SCN)]_2$ [19]; 2.481(4) and 2.461(4) Å in $(AgClP_2SC_{28}H_{28})_2$ [20]; 2.428(2) and 2.414(2) Å in $[Ag\{C_5(CO_2Me)_5\}(PPh_3)_2]$ [21].

TABLE IV. Selected Bond Distances (Å) and Angles (°)

Cation					
Ag–P(1)	2.472(2)	P(1)–C(1)	1.813(4)	P(3)–C(27)	1.815(3)
Ag–P(2)	2.476(2)	P(1)–C(7)	1.804(3)	P(3)–C(33)	1.790(5)
Ag–P(3)	2.479(2)	P(1)–C(13)	1.817(7)	P(3)–C(39)	1.825(6)
Ag–P(4)	2.463(2)	P(2)–C(14)	1.818(6)	P(4)–C(40)	1.805(6)
C(13)–C(14)	1.340(9)	P(2)–C(15)	1.807(5)	P(4)–C(41)	1.806(4)
C(39)–C(40)	1.325(7)	P(2)–C(21)	1.824(4)	P(4)–C(47)	1.808(3)
P(1)–Ag–P(2)	84.1(1)	Ag–P(1)–C(1)	115.8(2)	Ag–P(3)–C(27)	115.9(2)
P(1)–Ag–P(3)	123.8(1)	Ag–P(1)–C(7)	125.9(2)	Ag–P(3)–C(33)	122.9(2)
P(1)–Ag–P(4)	127.8(1)	Ag–P(1)–C(13)	104.0(2)	Ag–P(3)–C(39)	104.2(2)
P(2)–Ag–P(3)	117.8(1)	C(1)–P(1)–C(7)	103.2(2)	C(27)–P(3)–C(33)	104.7(2)
P(2)–Ag–P(4)	124.2(1)	C(1)–P(1)–C(13)	102.0(3)	C(27)–P(3)–C(39)	101.7(3)
P(3)–Ag–P(4)	83.9(1)	C(7)–P(1)–C(13)	102.7(3)	C(33)–P(3)–C(39)	105.0(3)
P(1)–C(13)–C(14)	123.5(5)	Ag–P(2)–C(14)	104.4(2)	Ag–P(4)–C(40)	105.2(2)
P(2)–C(14)–C(13)	122.2(5)	Ag–P(2)–C(15)	120.7(2)	Ag–P(4)–C(41)	125.1(2)
P(3)–C(39)–C(40)	123.2(5)	Ag–P(2)–C(21)	116.4(2)	Ag–P(4)–C(47)	114.5(2)
P(4)–C(40)–C(39)	122.9(5)	C(14)–P(2)–C(15)	104.1(3)	C(40)–P(4)–C(41)	104.8(3)
		C(14)–P(2)–C(21)	103.9(3)	C(40)–P(4)–C(47)	102.7(3)
		C(15)–P(2)–C(21)	105.3(2)	C(41)–P(4)–C(47)	102.2(2)
Anion					
Sn–C(53)	2.118(3)	Sn–O(4)	2.240(7)	N(2)–O(4)	1.183(14)
Sn–C(59)	2.130(4)	N(1)–O(1)	1.291(7)	N(2)–O(5)	1.242(16)
Sn–C(65)	2.125(3)	N(1)–O(2)	1.212(7)	N(2)–O(6)	1.162(17)
Sn–O(1)	2.276(4)	N(1)–O(3)	1.217(8)		
C(53)–Sn–C(59)	116.8(2)	O(4)–Sn–C(53)	91.4(2)	O(1)–N(1)–O(2)	118.9(6)
C(53)–Sn–C(65)	129.9(2)	O(4)–Sn–C(59)	88.6(2)	O(1)–N(1)–O(3)	118.3(6)
C(59)–Sn–C(65)	113.3(2)	O(4)–Sn–C(65)	90.5(2)	O(2)–N(1)–O(3)	122.8(6)
O(1)–Sn–C(53)	94.5(2)	O(1)–Sn–O(4)	171.8(3)	O(4)–N(2)–O(5)	120.3(11)
O(1)–Sn–C(59)	83.7(2)	Sn–O(1)–N(1)	116.5(4)	O(4)–N(2)–O(6)	111.5(11)
O(1)–Sn–C(65)	90.1(2)	Sn–O(4)–N(2)	124.3(7)	O(5)–N(2)–O(6)	127.1(12)

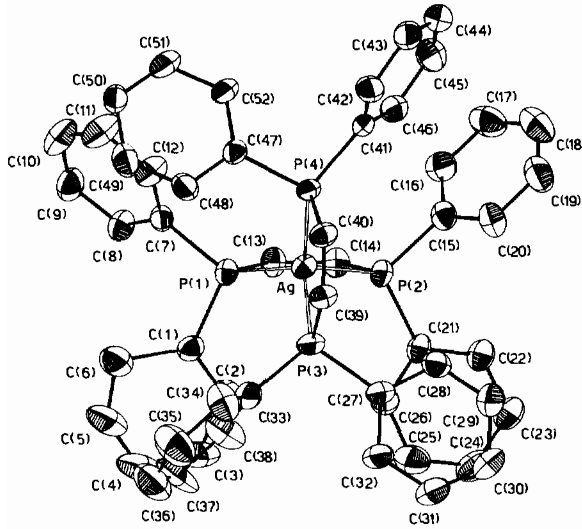

Fig. 1. Perspective view of the [Ag(cdppet)$_2$]$^+$ cation.

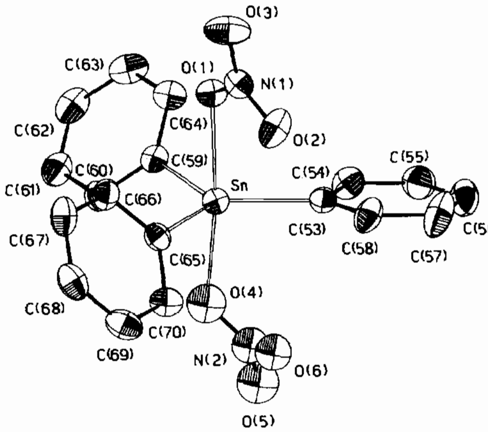

Fig. 2. Perspective view of the [SnPh$_3$(NO$_3$)$_2$] anion. The disorder in the N(2)O(4)O(5)O(6) nitrate group is not shown, for clarity.

As a consequence of chelation, two AgPCCP five-membered rings are formed, both of which adopt a Ag envelope conformation, with the remaining four atoms coplanar within experimental error. The two rings are approximately perpendicular to one another with a dihedral angle of 88.6(1)°. The out-of-plane distance of the P atoms from the phenyl rings varies from 0.05 to 0.27 Å. In each PPh$_2$ moiety, the planes of the two aromatic rings are inclined to each other at angles ranging from 68.61(1)° to 121.8(1)°. In both the cdppet molecules the bonding arrangement around the P atom is approximately tetrahedral with the angles subtended at P by Ag and C_{phenyl} spanning a wide range, 114.5(2)°–125.9(2)°, and all the remaining angles lying between 101.7(3)°–105.3(2)°.

In the anion the arrangement of the coordinated ligands around the tin atom is essentially trigonal bipyramidal. The equatorial plane of the bipyramid is defined by three phenyl carbon atoms, while two oxygen atoms from two unidentate nitrate groups occupy the axial positions. This analysis provides further evidence concerning the marked tendency of triphenyltin(IV) compounds to adopt a trigonal bipyramidal geometry with the rings being equatorial in accord with the propensity of electronegative ligands to assume axial positions. The tin atom is contained exactly in two phenyl planes, while it is slightly displaced (0.12 Å), probably for steric reasons, out of the C(65)–C(70) ring plane. The angles of twist of the aromatic rings with respect to the SnC_3 plane are 169.5(2)°, 131.5(1)° and 131.5(1)°, in numerical ordering by carbon atoms. The *trans* angle O–Sn–O is nearly linear at 171.8(3)°. The angle sum in the trigonal plane is 360.0°, but the individual values are further from 120° than would be expected (113.3(2)°–129.9(2)°). Angles formed by the axial atoms with the equatorial atoms are within 1.5° of 90°, with the exception of O(1)–Sn–C(53) (94.5(2)°) and O(1)–Sn–C(59) (83.7(2)°). The two Sn–O bond distances with values of 2.276(4) and 2.240(7) Å are quite similar and in excellent agreement with those reported for the corresponding bond in five-coordinated monomeric trigonal bipyramidal $SnPh_3(NO_3)X$ compounds containing monodentate nitrate groups in axial positions (Sn–O = 2.245(8), 2.22(2), and 2.274(6) Å for X = pyo, TPPO, and TPAO, respectively [22]. The three Sn–C bonds are of very similar length (2.118(3), 2.130(4), and 2.125(3) Å), and fall just in the middle of the range, 2.075–2.181 Å, observed for equatorial Sn–C bonds in five-coordinated trigonal bipyramidal triphenylderivatives (see Table VI, ref. 23). The values of Sn–O–N are consistent with a monodentate coordination of the nitrate ligand. In both cases there is a relatively close approach of a second oxygen atom to tin, the O...Sn contact amounting to *ca.* 3.10 Å.

The molecular packing is mainly governed by van der Waals interactions; the closest approach is 3.276(6) Å and occurs between C(43) of the asymmetric unit and O(3) at $x, y - 1, z - 1$.

Infrared Spectra

A comparison of the main vibrational bands of the silver–tin complex salts with those of the free cdppet and $Ag(cdppet)_2NO_3$ (Table V) reveals that the diphosphine ligand is slightly influenced by the coordination effect. The more significant absorptions concern the nitrate groups, whose stretching frequencies are strictly indicative of their ligand behaviour. As we have previously pointed out [3], the vibrational frequency values of the nitrate group can be discussed in the light of the X-ray data. In particular, the separation of the symmetric and asymmetric modes, $\Delta\nu = \nu_{as}(NO_3) - \nu_s(NO_3)$, provides evidence about the mono or bidentate mode of coordination of the nitrate group. The $\Delta\nu$ values in the spectra of $[Ag(cdppet)_2][SnPh_3(NO_3)_2]$ (170 cm^{-1}) and $[Ag(cdppet)_2][SnPh_2(NO_3)_3]$ (210 cm^{-1}) agree well with a monodentate and a bidentate ligand behaviour respectively [6, 24, 25]. As concerns $[Ag(cdppet)_2][SnPh_2(NO_3)Cl_2]$, the value of 183 cm^{-1} does not permit an unambiguous attribution.

NMR Spectra

^{119}Sn NMR spectra

A very important property of $\delta(^{119}Sn)$ is that an increase in coordination number of tin atom from four to five, six or seven usually produces a large upfield shift [26, 27]. This trend is observed also in the anions of $[Ag(cdppet)_2][SnPh_3(NO_3)_2]$ and $[Ag(cdppet)_2][SnPh_2(NO_3)Cl_2]$ (the other tin anion has not been examined owing to poor quantity). The chemical shift of the $[SnPh_3(NO_3)_2]^-$ ion (−263 ppm) where tin is pentacoordinated is remarkably at higher field than that of $SnPh_3Cl$ (−44.7 ppm) containing tetracoordinated tin. Morevoer its

TABLE V. Selected IR Bands (cm^{-1}) and Relative Assignments

	$\nu_{as}(NO_3)$	$\nu_s(NO_3)$	$\nu(NO_3)$		ν(Sn–C)
			in plane	out of plane	
$Ag(cdppet)_2NO_3$		1375s, br		828m	
$[Ag(cdppet)_2][SnPh_2(NO_3)_3]$	1490s	1280s	1012m	807w	295m
$[Ag(cdppet)_2][SnPh_3(NO_3)_2]$	1465s	1295s	1009m 1000sh	809m	265m
$[Ag(cdppet)_2][SnPh_2(NO_3)Cl_2]$ [a]	1470s	1287s		807w	290m

[a] ν(Sn–Cl) = 270 cm^{-1}.

chemical shift is in good agreement with those observed for other isostructural anions [28] such as $[SnPh_3Br_2]^-$ (−240 ppm) and $[SnPh_3Cl_2]^-$ (−257 ppm). In the $[SnPh_2(NO_3)Cl_2]^-$ ion the chemical shift moves further to higher field (−447 ppm), indicating that probably in solution the nitrato ligand behaves as bidentate, producing a distorted square bipyramidal environment around tin.

^{31}P *NMR*

$Ag(cdppet)_2NO_3$ and the tin containing compounds give the same $^{31}P\{^1H\}$ NMR spectrum, *i.e.* that of the silver cation $[Ag(cdppet)_2]^+$. At 233 K it consists of two doublets arising from $^{107}Ag-^{31}P$ and $^{109}Ag-^{31}P$ spin–spin coupling ($\delta(^{31}P)$, 4.2 ppm; $^1J(^{107}Ag, ^{31}P)$, 235.2 Hz; $^1J(^{109}Ag, ^{31}P)$, 271.5 Hz). At room temperature they collapse in one doublet owing to fast ligand exchange and only the average value of $^1J(Ag, P)$ is observable ($\delta(^{31}P)$, 2.0 ppm; $^1J_{av}(Ag, ^{31}P)$, 254 Hz). Lability of the phosphorus ligands in silver phosphine complexes has been previously evidenced and discussed [29]. The value of $^1J(^{107}Ag, ^{31}P)$ is well comparable with that observed for $Ag(PPh_3)_3I$ (262 Hz) [30], exhibiting tetrahedral coordination, and is significantly lower than those of trigonal silver compounds [31].

Conductivity Data

The nitrobenzene solution of all the complexes at room temperature (Table I) shows a molar conductivity approaching that of a 1:1 electrolyte. Conductivity measurements were carried out also on the previously structurally characterized $[Ag(AsPh_3)_4][SnPh_2(NO_3)_3]$, which also contains silver cations and tin anions [4]. The conductivity values observed in our complexes are low when compared to those reported in the literature [32] for 1:1 electrolytes ($\Lambda_M = 20–30$ ohm^{-1} cm^2 mol^{-1}) and this can be justified by the bulky nature of both the cation and the anion. In conclusion, we can assign an ionic nature to all the complexes of general formula $[Ag(cdppet)_2]^+[SnPh_{4-n}(NO_3)_nX]^-$ ($n = 1$, $X = NO_3$; $n = 2$, $X = Cl, NO_3$). This is further substantiated by the results of the structure determination.

Supplementary Material

Listing of thermal parameters, observed and calculated structure factors, and full bond length and angle data are available from the authors on request.

References

1 P. G. Harrison, N. W. Sharpe, C. Pelizzi, G. Pelizzi and P. Tarasconi, *J. Chem. Soc., Dalton Trans.*, 1687 (1983).

2 S. Dondi, M. Nardelli, C. Pelizzi, G. Pelizzi and G. Predieri, *J. Chem. Soc., Dalton Trans.*, 487 (1985).

3 S. Dondi, M. Nardelli, C. Pelizzi, G. Pelizzi and G. Predieri, *J. Organomet. Chem., 308,* 195 (1986).

4 M. Nardelli, C. Pelizzi, G. Pelizzi and P. Tarasconi, *J. Chem. Soc., Dalton Trans.*, 321 (1985).

5 C. Pelizzi, G. Pelizzi and P. Tarasconi, *J. Organomet. Chem., 277,* 29 (1984).

6 D. Franzoni, C. Pelizzi, G. Pelizzi, P. Tarasconi and F. Vitali, *Proc. of the 5th International Conference on the Organometallic and Coordination Chemistry of Germanium, Tin and Lead,* Padua, Italy, 1986, p. 108.

7 W. Levason and C. A. McAuliffe, *Inorg. Chim. Acta, 8,* 25 (1974).

8 D. V. Sanghani, P. J. Smith, D. W. Allen and B. F. Taylor, *Inorg. Chim. Acta, 59,* 203 (1982).

9 M. Barrow, H.-Bürgi, M. Camalli, F. Caruso, E. Fischer, L. M. Venanzi and L. Zambonelli, *Inorg. Chem., 22,* 2356 (1983).

10 T. N. Srivastava and M. P. Agarwal, *Indian J. Chem., 8,* 652 (1970).

11 C. Pelizzi, G. Pelizzi and P. Tarasconi, *Inorg. Chim. Acta, 40,* 183 (1980).

12 M. S. Lehmann and F. K. Larsen, *Acta Crystallogr., Sect. A, 30,* 580 (1974).

13 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A, 39,* 158 (1983).

14 'International Tables for X-Ray Crystallography', Vol. 4, Kynoch Press, Birmingham, 1974.

15 G. M. Sheldrick, 'SHELX-76', program for crystal structure determination, University of Cambridge, 1976.

16 D. Delledonne, G. Pelizzi and C. Pelizzi, *Acta Crystallogr., Sect. C, 43,* 1502 (1987).

17 L. M. Engelhardt, C. Pakawatchai, A. H. White and P. C. Healy, *J. Chem. Soc., Dalton Trans.*, 125 (1985).

18 P. F. Barron, J. C. Dyason, P. C. Healy, L. M. Engelhardt, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1965 (1986).

19 J. Howatson and B. Morosin, *Cryst. Struct. Commun., 2,* 51 (1973).

20 K. Aurivillius, A. Cassel and L. Fälth, *Chem. Scr., 5,* 9 (1974).

21 M. I. Bruce, M. L. Williams, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 799 (1983).

22 M. Nardelli, C. Pelizzi and G. Pelizzi, *J. Organomet. Chem., 125,* 161 (1977), and refs. therein.

23 M. Nardelli, C. Pelizzi and G. Pelizzi, *Inorg. Chim. Acta, 33,* 181 (1979), and refs. therein.

24 A. B. P. Lever, E. Mantovani and B. S. Ramaswamy, *Can. J. Chem., 49,* 1957 (1971).

25 D. Potts, H. D. Sharma, A. J. Carty and A. Walker, *Inorg. Chem., 13,* 1205 (1974).

26 A. G. Davies and P. J. Smith, in G. Wilkinson, F. G. A. Stone and E. W. Abel (eds.), 'Comprehensive Organometallic Chemistry', Vol. 2, Pergamon Press, Oxford, 1982, p. 527.

27 B. Wrackmeyer, *Annu. Rep. N.M.R. Spectrosc., 16,* 73 (1985).

28 J. Holeček, M. Nadvornik, K. Handliŕ and A. Lyc̀ka, *J. Organomet. Chem., 241,* 177 (1983).

29 E. L. Muetterties and C. W. Alegranti, *J. Am. Chem. Soc., 94,* 6386 (1972).

30 M. Camalli and F. Caruso, *Inorg. Chim. Acta, 127,* 209 (1987).

31 M. Camalli, F. Caruso, S. Chaloupka, P. N. Kapoor, P. S. Pregosin and L. M. Venanzi, *Helv. Chim. Acta, 67,* 1603 (1984).

32 W. J. Geary, *Coord. Chem. Rev., 7,* 81 (1971).