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Synthesis and structural characterization of triphenyltin halide-lactam complexes

Tadasu Tahara, Hideyuki Imazaki,
Nitto Kasei Co. Ltd., Higashiyodogawa, Osaka 533 (Japan)

Katsuyuki Aoki and Hiroshi Yamazaki
The Institute of Physical and Chemical Research, Wako, Saitama 351 (Japan)

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Abstract

Reactions of triphenyltin chloride or isothiocyanate with lactam yield complexes of the type $Ph_3SnX \cdot L$ (X = Cl or NCS, L = lactam). The coordination of the carbonyl group of lactams to the tin atom has been suggested by IR data and confirmed by X-ray diffraction analysis.

The crystal and molecular structure of triphenyltin chloride-ε-caprolactam complex, $C_{24}H_{26}ClNOSn$, has been determined by X-ray diffraction analysis. The crystals are orthorhombic, space group *Pbca*, *a* 18.839(1), *b* 14.392(2), *c* 29.059(6) Å, $Z = 8$; $R = 0.047$, $R_w = 0.058$ for 3579 unique reflections. The geometry around the tin atom is trigonal bipyramidal with the three phenyl groups defining the equatorial plane and a chlorine ion and a carbonyl oxygen of the caprolactam ligand occupying the axial positions.

Introduction

Organotin compounds, particularly triorganotin compounds have long been known for their biological activity and have found numerous applications in such diverse areas as marine-antifouling paints, agricultural chemicals, wood preservatives, bactericides and fungicides.

As to antifouling paints and coatings, their lifespan has been extended by including in the formulation organotin polymers, in which the tributyltin groups are chemically bound to the polymer backbone, e.g. poly(tributyltin methacrylate-methyl methacrylate) [1–8]. Prolonged efficiency is ensured by slow layer-by-layer dissolution of polymeric material thus providing a constant release of toxicant, with a self-polishing effect. Nowadays they are widely used for protecting the hulls of large ships.

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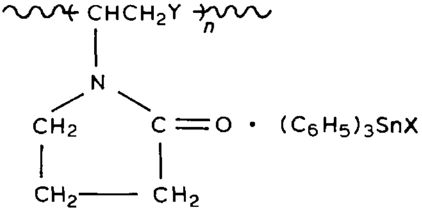

Fig. 1. Polymer A; X = halide or pseudohalide, Y = comonomer.

There have been some attempts to develop triphenyltin-containing polymers [9–11]. A variety of these including triphenyltin-methacrylate, -maleate, -itaconate and alkyd resin polymers have been studied. However, these polymers are subject to gelation in the presence of traces of water when additives are added during paint formulation. Gelation also takes place even if minute quantities of water are present in the polymerization system of the triphenyltin monomers. The partial hydrolysis of the polymers is considered to be responsible for the gelation. The carboxylic acid formed by the hydrolysis, breaks the tin–carbon bond of triphenyltin moiety to produce diphenyltin derivatives which cross-link the polymers thus leading to gelation.

Although there have been some reports [12,13] on the adducts of organotin compounds with amides such as DMF, no examples of triorganotin-lactam complexes have so far been found. Recently, we have prepared new polymers A (Fig. 1), containing triphenyltin halide- (or pseudohalide)-lactam complexes as the pendant group [14–16], and have found that they have efficient antifouling characteristics. However, details of the bonding between tin and lactam as well as its stability in various states were not known. So in order to obtain information about the bonding mode in the tin-lactam polymers we attempted to synthesize the monomeric compounds.

Here, we describe the synthesis of some triphenyltin chloride- (and isothiocyanate)-lactam complexes, and their structural analysis (by IR spectroscopy and X-ray crystallography).

Results and discussion

Synthesis of triphenyltin chloride- (or isothiocyanate)-lactam complexes (1–8)

The organotin halides and pseudohalides of the formula R_mSnX_{4-m} ($m = 1$–3) show a marked tendency to exceed tetra-coordination by forming complexes with Lewis bases. The acceptor ability of the organotin compounds R_mSnX_{4-m} generally increases (a) as the electronegativity of the substituents (R and X) increases, and (b) as the number (m) of R-substituents decreases [17].

It is well known that triorganotin halides R_3SnX are weak acceptors and favor an increase in the coordination number to five of the tin atom by reaction with a donor ligand to form trigonal-bipyramid complexes. We have now found that lactams such as 2-pyrrolidone, valerolactam and ϵ-caprolactam are efficient Lewis bases that are able to coordinate triphenyltin halides.

The synthesis of triphenyltin chloride-lactam complexes as readily achieved by mixing equimolar amounts of triphenyltin chloride and the corresponding lactam in

Table 1

Melting points and IR data for the complexes [a]

Complex	M.p. (°C)	ν(C=O) (KBr disk) (cm^{-1})	$\Delta\nu$(C=O) [b] (cm^{-1})
Ph_3SnCl·2-pyrrolidone (**1**)	73– 74	1648	30
Ph_3SnCl·*N*-methylpyrrolidone (**2**)	100–105	1632	40
Ph_3SnCl·valerolactam (**3**)	86– 87	1622	36
Ph_3SnCl·ε-caprolactam (**4**)	80– 81	1620	40
Ph_3SnNCS·2-pyrrolidone (**5**)	113–114	1640	38
Ph_3SnNCS·*N*-methylpyrrolidone (**6**)	130–132	1628	44
Ph_3SnNCS·valerolactam (**7**)	127–128	1614	44
Ph_3SnNCS·ε-caprolactam (**8**)	105–106	1616	44

[a] ν(C=O) of free lactams: 2-pyrrolidone (1678 cm^{-1}), *N*-methylpyrrolidone (1672 cm^{-1}), valerolactam (1658 cm^{-1}, 1642 cm^{-1}), ε-caprolactam (1660 cm^{-1}). [b] $\Delta\nu(C{=}O) = [\nu(C{=}O)_{free} - \nu(C{=}O)_{complex}]$.

cyclohexane under reflux. After cooling to room temperature, the separated product was collected, and recrystallized from cyclohexane to give the lactam complex in high yields. Triphenyltin isothiocyanate complexes were prepared analogously.

The elemental analyses showed that all complexes have a 1 : 1 composition of tin and lactam. The melting points of the new complexes (**1**–**8**) obtained are shown in Table 1.

IR spectra

The formation of triphenyltin derivative-lactam complexes is confirmed by a shift to lower frequencies of the band due to the carbonyl stretching vibrations of the coordinated lactam molecules. The ν(C=O) absorption bands of compounds **1** to **8** in the solid state (KBr disk) are shown in Table 1 along with those of the corresponding free lactame.

The IR data indicate that when the complexes are formed ν(C=O) bands of the complexes are lowered by 30–44 cm^{-1} compared with those of the corresponding free lactam. This fact indicates that the coordination of the lactam to the tin atom is through the oxygen of the carbonyl group. The generalization that the larger the magnitude of $\Delta\nu$(C=O) for a given carbonyl ligand, the stronger the donor interaction [18] would indicate that triphenyltin isothiocyanate is a stronger acceptor than the chloride as expected.

To confirm the structures of the complexes, the molecular structure of triphenyltin chloride-ε-caprolactam was investigated by X-ray crystallography.

Crystal structure of the triphenyltin chloride-ε-caprolactam complex 4

The molecular structure of the complex with atom numbering scheme is shown in Fig. 2; selected bond distances and angles are listed in Table 2. The geometry around the tin atom is trigonal bipyramidal, which is usual for five-coordinate triphenyltin compounds [19]. The three phenyl groups define the equatorial plane, with the chlorine and carbonyl oxygen of the caprolactam ligand occupying the axial positions. The tin atom deviates by 0.200(4) Å from the plane (consisting of the three phenyl ring atoms [C(11), C(21), C(31)]) towards the chlorine atom, with the phenyl ring planes inclined at 63.6 [ring C(11)–C(16)], 35.9 [ring C(21)–C(26)], and 48.5° [ring C(31)–C(36)] to the SnC_3 plane. The caprolactam ligand is arranged

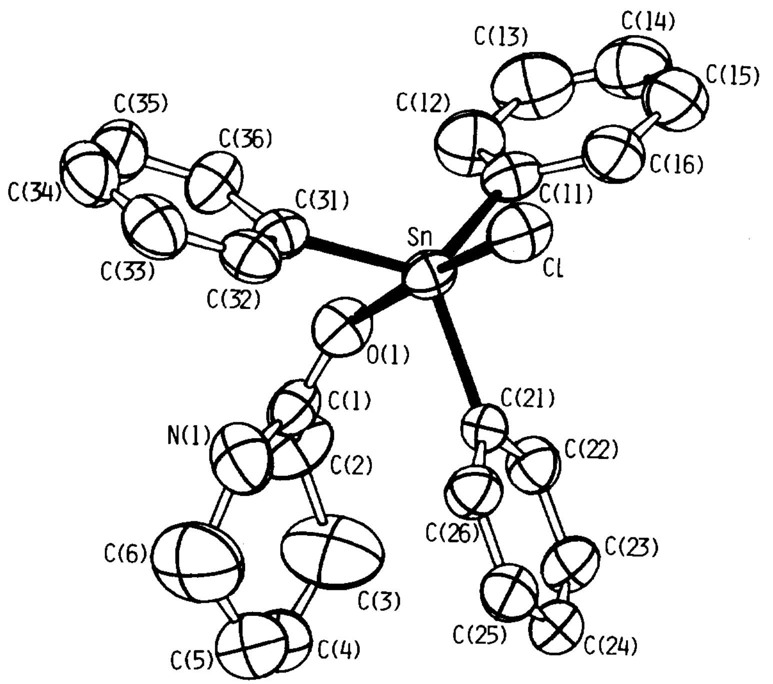

Fig. 2. Molecular structure of the triphenyltin chloride·ϵ-caprolactam complex 4. The atoms are shown as 50% probability spheres.

such that it is in close contact with the phenyl ring [C(21)–C(26)]; intramolecular close-contacts < 3.5 Å are O(1) ··· C(12) = 3.043(8), O(1) ··· C(22) = 3.189(8), O(1) ··· C(36) = 3.171(8), C(1) ··· C(21) = 3.359(8), C(1) ··· C(22) = 3.384(9) and N(1) ··· C(21) = 3.456(8) Å, while C(1) ··· C(31) = 3.762(8) and N(1) ··· C(31) = 3.621(9) Å. Molecular dimensions within the coordination sphere are comparable with those in compounds having a trigonal-bipyramidal $SnPh_3ClO$ core, with small but significant differences in the Sn–O and Sn–Cl distances; values found for the seven compounds are compared in Table 3. The Sn–O bond distance seems to be sensitive to steric effects, since the apical ligation site is spacially restricted by the inclining phenyl groups. Thus relatively small values of the Sn–O distance in the arsine oxide [20] or phosphine oxide [21,22] compounds are compensated for by the large O–As or O–P distances thus avoiding steric constraint between coordinated phenyl groups and As- or P-attached phenyl groups, however, this trend is reversed for the present caprolactam or tetramethylurea [25] compound. In the case of the carboxylated compound [24], the carboxylate group has sufficient separation to avoid pyridinium-phenyl steric hindrance. One exception is the sulfoxide compound [23] which, in contrast to our expectation, has a large Sn–O separation probably owing to the disorder of the n-propyl groups.

This is only the third crystal structure of metal ions with a lactam, and the first with triphenyltin chloride ever determined; the other two are tris(octanelactam)chromium(III) trichloride [26] and hexakis(ϵ-caprolactam)copper(II) bis[trichloro(ϵ-caprolactam)copper(II)] [27]. In these three compounds, the amide oxygen occupies a unique ligation site. The caprolactam ligand adopts a chair

Table 2

Heavy-atom bond lengths (Å) and angles (°) in $Ph_3SnCl\cdot\epsilon$-caprolactam

(a) Coordination sphere			
Sn–Cl	2.485(2)	Sn–C(21)	2.146(6)
Sn–O(1)	2.399(4)	Sn–C(31)	2.142(6)
Sn–C(11)	2.125(6)	Sn···N(1)	3.685(7)
Cl–Sn–O(1)	175.9(1)	O(1)–Sn–C(21)	83.4(2)
Cl–Sn–C(11)	98.6(2)	O(1)–Sn–C(31)	86.1(2)
Cl–Sn–C(21)	92.7(2)	C(11)–Sn–C(21)	113.2(2)
Cl–Sn–C(31)	94.8(2)	C(11)–Sn–C(31)	121.6(2)
O(1)–Sn–C(11)	84.3(2)	C(21)–Sn–C(31)	122.6(2)
(b) ε-Caprolactam ligand			
C(1)–C(2)	1.469(9)	C(5)–C(6)	1.445(16)
C(2)–C(3)	1.489(13)	C(6)–N(1)	1.463(13)
C(3)–C(4)	1.466(15)	N(1)–C(1)	1.354(10)
C(4)–C(5)	1.477(13)	C(1)–O(1)	1.256(8)
Sn–O(1)–C(1)	130.2(4)	C(5)–C(6)–N(1)	121.9(10)
C(1)–C(2)–C(3)	118.8(7)	C(6)–N(1)–C(1)	127.8(7)
C(2)–C(3)–C(4)	119.7(10)	N(1)–C(1)–C(2)	119.5(6)
C(3)–C(4)–C(5)	120.3(8)	N(1)–C(1)–O(1)	122.2(6)
C(4)–C(5)–C(6)	116.3(9)	C(2)–C(1)–O(1)	118.2(6)
(c) Phenyl ligands			
C(11)–C(12)	1.385(11)	C(24)–C(25)	1.385(11)
C(12)–C(13)	1.426(12)	C(25)–C(26)	1.391(10)
C(13)–C(14)	1.356(14)	C(26)–C(21)	1.372(9)
C(14)–C(15)	1.370(13)	C(31)–C(32)	1.371(9)
C(15)–C(16)	1.408(12)	C(32)–C(33)	1.406(11)
C(16)–C(11)	1.369(10)	C(33)–C(34)	1.344(12)
C(21)–C(22)	1.396(9)	C(34)–C(35)	1.362(12)
C(22)–C(23)	1.384(10)	C(35)–C(36)	1.390(15)
C(23)–C(24)	1.345(10)	C(36)–C(31)	1.384(10)
Sn–C(11)–C(12)	122.8(6)	C(21)–C(22)–C(23)	120.8(6)
Sn–C(11)–C(16)	119.6(5)	C(22)–C(23)–C(24)	120.4(7)
Sn–C(21)–C(22)	118.8(4)	C(23)–C(24)–C(25)	120.4(7)
Sn–C(21)–C(26)	123.2(5)	C(24)–C(25)–C(26)	119.3(7)
Sn–C(31)–C(32)	122.4(5)	C(25)–C(26)–C(21)	121.1(6)
Sn–C(31)–C(36)	119.5(5)	C(26)–C(21)–C(22)	118.0(6)
C(11)–C(12)–C(13)	121.1(8)	C(31)–C(32)–C(33)	120.7(7)
C(12)–C(13)–C(14)	119.3(8)	C(32)–C(33)–C(34)	120.5(7)
C(13)–C(14)–C(15)	121.0(8)	C(33)–C(34)–C(35)	119.4(7)
C(14)–C(15)–C(16)	118.9(8)	C(34)–C(35)–C(36)	121.1(8)
C(15)–C(16)–C(11)	122.4(7)	C(35)–C(36)–C(31)	120.1(7)
C(16)–C(11)–C(12)	117.4(7)	C(36)–C(31)–C(32)	118.1(6)

conformation with an approximate mirror passing through C(4) and the midpoint of the N(1)–C(1) bond, as is the case for the metal-free ε-caprolactam molecule [28]; torsion angles are listed in Table 4. The amide group and the C(2) and C(6) atoms are approximately planar with torsion angles C(2)–C(1)–N(1)–C(6) = 11(1) and O(1)–C(1)–N(1)–C(6) = −169.6(8)°. Most of the bond lengths and angles of the caprolactam ligand are normal as expected [27,28] (Table 2). Unfortunately, limited accuracy of the present analysis precludes detailed discussion of the effects of

Table 3

Comparison of the molecular dimensions within the trigonal-bipyramidal $SnPh_3Cl(O{=}X-)$ [X = C, P, S or As] core

Compound	Bond distance (Å)				Bond angle (°)	Ref.
	$Sn-C_{mean}$	Sn–O	Sn–Cl	O–X	Sn–O–X	
$(SnPh_3Cl)_2$[1,2-bis-(diphenylarsonyl)-ethane]	2.117(8)	2.239(4)	2.532(2)	1.665(4) (X = As)	134.5(2)	20
$SnPh_3Cl$[*cis*-1,2-bis-(diphenylphosphinyl)-ethylene]	2.142(16)	2.346(6)	2.489(3)	1.496(7) (X = P)	141.2(4)	21
$(SnPh_3Cl)_2$[bis-(diphenylphosphinyl)-ethane]	2.123(9)	2.357(3)	2.475(2)	1.487(3) (X = P)	161.8(2)	22
$SnPh_3Cl$[*rac*-1,2-bis-(n-propylsuphinyl)-ethylene]	2.125(4)	2.447(6)	2.484(2)	1.484(2) (X = S)	128.8(5)	23
$SnPh_3Cl$(pyridinium--2-carboxylate)	2.135(7)	2.347(3)	2.515(1)	1.256(5) (X = C)	135.3(1)	24
$SnPh_3Cl$-(tetramethylurea)	2.13(2)	2.383(8)	2.485(4)	1.26(2) (X = C)	136.8(8)	25
$SnPh_3Cl$-(ϵ-caprolactam)	2.138(11)	2.399(4)	2.485(2)	1.256(8) (X = C)	130.2(4)	This work

Table 4

Torsion angles (°) in the ϵ-caprolactam ligand

C(1)–C(2)–C(3)–C(4)	67.3(12)
C(2)–C(3)–C(4)–C(5)	−53.6(13)
C(3)–C(4)–C(5)–C(6)	53.9(13)
C(4)–C(5)–C(6)–N(1)	−65.0(14)
C(5)–C(6)–N(1)–C(1)	46.7(15)
C(6)–N(1)–C(1)–C(2)	10.7(12)
N(1)–C(1)–C(2)–C(3)	−58.6(10)
C(3)–C(2)–C(1)–O(1)	121.7(8)
C(6)–N(1)–C(1)–O(1)	−169.6(8)

ligation on the molecular dimensions of the amide group. The thermal parameters of C(3), C(5), and C(6) are somewhat larger than those for C(1), C(2), C(4), and N(1) and this may imply some sort of minor disorder in the packing of the molecules, reflecting rather short bond distances for these atoms.

The crystal packing is dominated by van der Waals interactions, the shortest contact being C(2) $\cdots$ C(14) $(1-x, 1/2-y, -z)$ 3.58(1) Å.

Experimental

Materials

Triphenyltin chloride (available in technical grades from Nitto Kasei Co. Ltd.) was purified by recrystallization from cyclohexane before use (purity: 99.7%). The lactams used as purchased. Solvents were distilled before use.

Preparation of triphenyltin isothiocyanate

Triphenyltin isothiocyanate was prepared by the method described in ref. 31. M.p. 169–170 °C (lit., 168–170.5 °C).

Preparation of the tin-lactam complexes

Triphenyltin chloride-ϵ-caprolactam complex 4. A reaction vessel was charged with cyclohexane (100 ml), triphenyltin chloride (38.5 g, 0.1 mol) and ϵ-caprolactam (11.3 g, 0.1 mol). The reaction mixture was heated under reflux for 1 h with stirring. Then the hot solution was filtered and the filtrate was allowed to stand at room temperature, giving colorless crystals in 78% yield. Recrystallization of the crude product from cyclohexane afforded colorless needles, 80–81 °C. Found: C, 58.15; H, 5.27; N, 2.99; Cl, 6.88; Sn, 23.61. $C_{24}H_{26}ClNOSn$ calc: C, 57.81; H, 5.26; N, 2.81; Cl, 7.11; Sn, 23.80%.

Complexes **1**–**3** were prepared similarly viz. reaction of triphenyltin chloride with lactam.

Complex 1. Found: C, 55.85; H, 4.73; N, 3.07; Sn, 25.24. $C_{22}H_{22}ClNOSn$ calc: C, 56.15; H, 4.71; N, 2.98; Cl, 7.53; Sn, 25.22%.

Complex 2. Found: C, 57.32; H, 5.08; N, 2.69; Cl, 7.24; Sn, 24.45. $C_{23}H_{24}ClNOSn$ calc: C, 57.01; H, 4.99; N, 2.89; Cl, 7.32; Sn, 24.49%.

Complex 3. Found: C, 57.11; H, 4.97; N, 2.86; Cl, 7.36; Sn, 24.25. $C_{23}H_{24}ClNOSn$ calc: C, 57.01; H, 4.99; N, 2.89; Cl, 7.32; Sn, 24.49%.

Triphenyltin isothiocyanate-2-pyrrolidone complex 5. To a solution of triphenyltin isothiocyanate (20.41 g, 0.05 mol) in 2-propanol (55 ml) was added 2-pyrrolidone (4.26 g, 0.05 mol). The reaction mixture was stirred at room temperature for 30 min and cooled in an ice bath to give colorless needles (yield 95%; m.p., 113–114 °C), these (2 g) were recrystallized from cyclohexane (250 ml) to give colorless needles (1.92 g; m.p., 114–115 °C). Found: C, 55.92; H, 4.26; N, 5.57; Sn, 24.15. $C_{23}H_{22}N_2OSSn$ calc: C, 56.01; H, 4.49; N, 5.67; Sn, 24.07%.

Complex 8. Found: C, 57.66; H, 4.83; N, 5.43; Sn, 22.95. $C_{25}H_{26}N_2OSSn$ calc.: C, 57.82; H, 5.02; N, 5.39; Sn, 22.77%.

Triphenyltin isothiocyanate-N-methyl pyrrolidone complex 6. To a solution of triphenyltin isothiocyanate (8.16 g, 0.02 mol) in diethyl ether (125 ml) was added a solution of *N*-methyl pyrrolidone (2.10 g, 0.021 mol) in diethyl ether (12 ml) with stirring at room temperature, and after a short time crystals separated out (yield 92.0%). The crystals (1.5 g) were recrystallized from cyclohexane (120 ml) to give colorless needles (m.p., 141–143 °C). Found: C, 56.55; H, 4.55; N, 5.49; Sn, 23.75. $C_{24}H_{24}N_2OSSn$ calc.: C, 56.83; H, 4.76; N, 5.52; Sn, 23.40%.

Complex 7. Found: C, 56.90; H, 4.93; N, 5.69; Sn, 23.39. $C_{24}H_{24}N_2OSSn$ calc: C, 56.83; H, 4.76; N, 5.52; Sn, 23.40%.

IR spectral data

IR spectral data was recorded on a Hitachi 270-30 spectrometer.

X-ray diffraction analysis of the triphenyltin chloride-ϵ-caprolactam complex (4)

Cell constants were determined from 20 high-order reflections ($24 < 2\theta(\text{Mo-}K_\alpha) < 34°$) on a Rigaku automated diffractometer. Details of crystal data collection and structure refinement are summarized in Table 5. The crystal was mounted such that the *a* axis was parallel to the ϕ axis of the diffractometer. Throughout data

Table 5

Cyrstal data and experimental details

Compound	$SnPh_3Cl \cdot (\epsilon$-caprolactam)
Formula	$C_{24}H_{26}ClNOSn$
fW	498.621
a (Å)	18.839(1)
b (Å)	14.392(2)
c (Å)	29.059(6)
V (Å^3)	4533(1)
Z	8
Space group	*Pbca*
Systematic reflection absences	$hk0$, $h = 2n+1$; $0kl$, $k = 2n+1$; $h0l$, $l = 2n+1$
Density, g cm^{-3}	1.461 (calc)
Cryst shape and dimensions	rectangular parallelepipeds; 0.619 × 0.407 × 0.326 mm
$F(000)$, electrons	2016
Radiation	Mo-K_α ($\lambda = 0.71073$ Å, graphite monochromator)
Temperature, (°C)	23
μ(Mo-K_α), (cm^{-1})	12.62
Transmission factors	0.96–1.04 [a]
Scan speed, (°)	4.0 in 2θ/min
Scan range, (°)	$1.2 + 0.5 \tan\theta$
Background counting, (s)	5 at the lower and upper limits of each scan
2θ limits, (°)	3.0–55.0
Scan mode	ω scan for $2\theta \leq 30.0°$ ω–2θ scan for $2\theta > 30.0°$
Diffractometer	Rigaku
Unique data measured	5522
Unique data (NO) used ($F_o > 3\sigma(F_o)$)	3579
Final no. of variables (NV)	314
R [b]	0.047
R_{wF} [c]	0.058
GOF [d]	2.91

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[a] Normalized to an average of 1. [b] $R = \Sigma | F_o - | F_c || / \Sigma F_o$. [c] $R_{wF} = [\Sigma w | F_o - | F_c ||^2 / \Sigma w F_o^2]^{1/2}$. [d] $GOF = [\Sigma w(F_o - | F_c |)^2 / (NO - NV)]^{1/2}$.

collection the intensities of three standard reflections were measured after every 100 reflections as a check of the stability of the crystal and the instrument; maximum variation in intensity of less than 2% was noted, and no decay correction was applied to the data. Intensities were corrected for Lorenz and polarization effects. The anisotropy of absorption was checked for the 600 axial reflections ($\chi = 90°$) in 15° steps of ϕ, and the crystal showed transmission factors (normalized to an average of 1) varying from 0.96 to 1.04, and no correction was made for absorption.

The space group *Pbca* was uniquely determined from the systematic absences. The structure was solved by Patterson and Fourier methods and refined by the block-diagonal least-squares method [29]. All non-hydrogen atoms were anisotropically refined, the function $\Sigma w(F_o - | F_c |)^2$ being minimized. All 15 hydrogen atoms attached to the three phenyl rings, were located from the difference Fourier map and were refined isotropically. The final R and R_{wF}, and the goodness of fit (GOF) values were 0.047, 0.058, and 2.9, respectively, for 3579 reflections (NO) and 314 variables (NV), from which $NO/NV = 11.4$. The weighting scheme suggested by

Table 6

Final heavy-atom parameters for $Ph_3SnCl \cdot \epsilon$-caprolactam[a]

Atom	x	y	z	B_{eq} (Å^2)
Sn	10406(4)	21484(3)	10869(1)	3.58(0.02)
Cl	−901(2)	2970(1)	1290(1)	5.02(0.08)
O(1)	2957(4)	1363(3)	948(2)	4.7(0.1)
C(1)	3644(5)	922(4)	1219(2)	4.2(0.2)
C(2)	4980(6)	939(6)	1136(3)	5.9(0.2)
C(3)	5808(8)	1297(9)	1504(4)	9.6(0.4)
C(4)	5936(8)	778(6)	1936(3)	6.7(0.3)
C(5)	4832(9)	519(7)	2204(3)	7.3(0.3)
C(6)	3883(12)	15(9)	1960(4)	10.7(0.4)
N(1)	3192(6)	434(5)	1580(3)	6.3(0.2)
C(11)	1498(6)	2906(5)	483(2)	4.3(0.2)
C(12)	2257(8)	2553(6)	142(3)	6.3(0.2)
C(13)	2637(9)	3113(7)	−237(3)	7.4(0.3)
C(14)	2282(8)	4016(7)	−255(3)	6.8(0.3)
C(15)	1526(9)	4384(6)	77(3)	6.8(0.3)
C(16)	1139(8)	3814(5)	443(3)	5.6(0.2)
C(21)	1975(5)	2643(4)	1690(2)	3.3(0.1)
C(22)	3118(6)	3078(4)	1640(2)	4.3(0.2)
C(23)	3751(6)	3409(5)	2019(3)	5.0(0.2)
C(24)	3295(7)	3286(6)	2445(2)	5.2(0.2)
C(25)	2166(8)	2854(3)	2509(2)	5.5(0.2)
C(26)	1511(6)	2542(5)	2127(2)	4.7(0.2)
C(31)	206(5)	802(4)	1052(2)	3.8(0.1)
C(32)	−691(6)	521(5)	1355(2)	4.6(0.2)
C(33)	−1238(7)	−361(6)	1314(3)	5.8(0.2)
C(34)	−897(7)	−942(5)	974(3)	6.1(0.2)
C(35)	2(8)	−676(5)	675(3)	6.1(0.2)
C(36)	565(6)	188(5)	711(3)	4.9(0.2)

[a] Positional parameters are $\times 10^5$ for Sn atom and $\times 10^4$ for other atoms. Equivalent temperature factors $B_{eq} = 4/3\Sigma_i\Sigma_j\beta_{ij}a_i \cdot a_j$.

Hughes [30] was used; $w = 1.0$ for $F_o \leq 100.0$ and $w^{1/2} = 100.0/F_o$ for $F_o \geq 100.0$; no systematic variation was observed in an analysis of $\Sigma w(F_o - |F_c|)^2$ as a function of either F_o or $\sin\theta/\lambda$. A final difference Fourier map showed no other features with absolute values greater than 0.6 e Å^{-3} near the tin position. Final heavy-atom parameters for **4** are given in Table 6.

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