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# Organotin esters of 3-ureidopropionic acid. Crystal structure of triphenyltin(IV) 3-ureidopropionate, $(C_6H_5)_3SnOCO(CH_2)_2NHCONH_2$

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## Abstract

Syntheses and spectroscopic ($^{119m}$Sn Mössbauer and infrared) data are reported for triorganotin derivatives of 3-ureidopropionic acid of the general formula, $R_3SnOCOCH_2CH_2NHCONH_2$ (R = Ph, $^n$Bu, cyclohexyl, and *p*-tolyl) and $Ph_2RSnOCOCH_2CH_2NHCONH_2$ (R = $^n$Bu, *p*-$ClC_6H_4$ and cyclopentyl). The crystal structure of triphenyltin 3-ureidopropionate has been determined. The compound adopts a *trans*-$C_3SnO_2$ trigonal bipyramidal geometry with the axial positions occupied by the ester oxygen and the ureido-oxygen of an adjacent molecule. The polymer units are held together by intermolecular hydrogen bonding between the group NH of the ureido fragment and the oxygen of the carboxylate carbonyl.

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## Introduction

Triorganotin(IV) carboxylates are generally five-coordinate carboxylate-bridged polymers in which the units are arranged in a zig-zag or helical manner in the crystal lattice [1,2]. Alternative bonding modes to carboxyl bridging have been sought in compounds containing donor substituent groups in the ester function, and among the earliest compound investigated was trimethyltin glycinate [3] whose crystal structure revealed a polymeric network built of Sn–N linkages. This feature has also been observed in triphenyltin pyridine-3-carboxylate [4], but not in triphenyltin 8-quinolyloxyacetate, where intermolecular hydrogen-bonding interactions between a coordinated water molecule and the quinolyloxyacyl O and N atoms effectively preclude the occurence of either Sn–O or Sn–N bridges [5]. Carboxylate bridging is, however, retained in triphenyltin 3-benzoylpropionate [6] whose ketonic oxygen atom is free. Similarly, the doubly-bonded sulfur atom in *N*-methyl-*N*-phenyldi-

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thiocarbamylacetato ligand is not involved in coordination to tin in the tri-n-butyltin ester, which is carboxylate-bridged [7]. Although two amide oxygen atoms are present in the *N*-phthaloylglycinate ligand, which are both more basic than the carboxylate oxygens, Sn–O bridges are found in triphenyltin *N*-phthaloylglycinate, and such bridging is lost only upon introduction of a bulky substituent such as iso-butyl at the $\alpha$-carbon of the ligand [8].

We describe here the synthesis and the characterisation by Mössbauer and infrared spectroscopic techniques of a series of triorganotin derivatives of 3-ureidopropionic acid, $NH_2CONHCH_2CH_2COOH$, a ligand which contains a potential bonding site in its ureido fragment in addition to the carboxyl function that could engage the tin atom in either intra- or inter-molecular (polymeric) coordination. Definitive establishment of the bonding behaviour in this class of compounds must come from X-ray diffraction studies, and we therefore carried out an X-ray crystal structure determination on a representative compound in the series, namely triphenyltin 3-ureidopropionate.

## Experimental

### *Reagents*

3-Ureidopropionic acid, triphenyltin hydroxide, bis(tributyltin) oxide, and tricyclohexyltin hydroxide were commercial chemicals of reagent-grade quality and were used without further purification. Tri(*p*-tolyl)tin hydroxide, m.p. 108–109 ° C, was prepared by vigorously stirring an ethereal solution of tri(*p*-tolyl)tin chloride (prepared from by comproportionation reaction of tetra(*p*-tolyl)tin and tin tetrachloride) with 5 *M* aqueous sodium hydroxide. Upon work-up, the ether layer yielded the crude hdyroxide, which was recrystallised from ethanol (77% yield). Diphenylbutyltin hydroxide, m.p. 282–284 ° C, was similarly prepared from diphenylbutyltin bromide [9]. Diphenyl(*p*-chlorophenyl)tin hydroxide was prepared as follows:

A mixture of triphenyl(*p*-chlorophenyl)tin (30 g, 68.0 mmol), iodine (17.1 g, 68 mmol), and 50 mL DMF was stirred at room temperature for 2 days until analysis of the mixture by TLC (silica gel; hexane–acetone (10 : 7 v/v), 0.1% ethanolic pyrocatechol violet spraying agent) indicated the absence of the tetraorganotin compound. Subsequently 35% $NH_4OH$ (20 mL) and acetone (20 mL) were added, and after overnight stirring the mixture was poured into 1 L of water, and after 2 h stirring the white solid formed was filtered off and air-dried. The solid was dissolved in chloroform and the solution dried over anhydrous $CaCl_2$. The chloroform solution was then filtered, and the solvent completely removed. The residue was taken up in 20 mL methanol, and the methanol solution was filtered and concentrated to give the pure hydroxide, m.p. 109–110 ° C, in 85% yield (23 g). Anal. Found: C, 54.06; H, 3.83. $C_{18}H_{15}ClOSn$ calcd.: C, 53.80; H, 3.74%.

A similar procedure gave diphenylcyclopentyltin hydroxide, m.p. 93–95 ° C, from triphenylcyclopentyltin in 82% yield. Anal. Found: C, 56.59; H, 5.69. $C_{17}H_{20}OSn$ calcd.: C, 56.82; H, 5.57%.

### *Preparation of triorganotin 3-ureidopropionates*

These were all prepared by the method detailed below for triphenyltin 3-ureidopropionate. A mixture of triphenyltin hydroxide and 3-ureidopropionic acid in

Table 1

Analytical data for triorganotin 3-ureidopropionates

| Compound [a] | M.p. (°C) | Analyses (Found (calcd.) (%)) | | |
|---|---|---|---|---|
| | | C | H | N |
| $Ph_3SnOCOCH_2CH_2NHCONH_2$ | 186–188 | 54.90 | 4.53 | 5.70 |
| | | (54.89) | (4.57) | (5.82) |
| $(^nBu)_3SnOCOCH_2CH_2NHCONH_2$ | 73– 74 | 45.80 | 8.37 | 6.64 |
| | | (45.61) | (8.08) | (6.65) |
| $(^cC_6H_{11})_3SnOCOCH_2CH_2NHCONH_2$ | 145–146 | 53.00 | 8.33 | 5.46 |
| | | (52.91) | (8.02) | (5.61) |
| ($p$-tolyl)$_3SnOCOCH_2CH_2NHCONH_2$ | 181–183 | 56.80 | 5.33 | 5.17 |
| | | (57.36) | (5.35) | (5.35) |
| $Ph_2(^nBu)SnOCOCH_2CH_2NHCONH_2$ | 154–156 | 51.30 | 5.56 | 5.77 |
| | | (52.06) | (5.64) | (6.07) |
| ($p$-ClPh)$Ph_2SnOCOCH_2CH_2NHCONH_2$ | 196–198 | 51.25 | 4.07 | 5.41 |
| | | (51.21) | (4.07) | (5.43) |
| $(^cC_5H_9)Ph_2SnOCOCH_2CH_2NHCONH_2$ | 179–181 | 53.40 | 5.27 | 5.83 |
| | | (53.28) | (5.50) | (5.92) |

[a] $^cC_6H_{11}$ = cyclohexyl, $^cC_5H_9$ = cyclopentyl.

1 : 1 molar ratio was heated in ethanol to form a clear solution. The pure product separated out when the solvent was allowed to evaporate off slowly. A single crystal of the compound suitable for X-ray crystallography was obtained by recrystallization from ethanol. The analytical data for the seven triorganotin 3-ureidopropionates are given in Table 1.

### *Mössbauer spectra*

The tin-119m Mössbauer spectra (Table 2) were obtained at 80 K with a Cryophysics constant acceleration spectrometer operating in the sawtooth wave mode. The velocity calibration was based on the room temperature spectrum of natural iron, with calcium stannate set to be the zero-velocity reference [10].

### *Infrared spectra*

The infrared spectra of the compounds were recorded with a Perkin Elmer 1700 FT-IR spectrophotometer, both as Nujol mulls between KBr plates and as chloroform solutions in polyethylene cells. The infrared data are listed in Table 3.

Table 2

Mössbauer data [a] for triorganotin 3-ureidopropionates at 80 K (mm $s^{-1}$)

| Compound | IS [b] | QS | $\Gamma_1$ | $\Gamma_2$ |
|---|---|---|---|---|
| $Ph_3SnOCOCH_2CH_2NHCONH_2$ | 1.22 | 3.12 | 0.86 | 0.86 |
| $(^nBu)_3SnOCOCH_2CH_2NHCONH_2$ | 1.51 | 3.41 | 0.90 | 0.92 |
| $(^cC_6H_{11})_3SnOCOCH_2CH_2NHCONH_2$ | 1.43 | 3.62 | 0.87 | 0.88 |
| ($p$-tolyl)$_3SnOCOCH_2CH_2NHCONH_2$ | 1.21 | 3.06 | 0.88 | 0.86 |
| $Ph_2(^nBu)SnOCOCH_2CH_2NHCONH_2$ | 1.40 | 3.48 | 0.91 | 0.93 |
| $Ph_2$($p$-ClPh)$SnOCOCH_2CH_2NHCONH_2$ | 1.23 | 3.38 | 0.88 | 0.88 |
| $Ph_2(^cC_5H_9)SnOCOCH_2CH_2NHCONH_2$ | 1.26 | 3.17 | 0.91 | 0.93 |

[a] Error ±0.05 mm $s^{-1}$. [b] Relative to $CaSnO_3$.

Table 3

Infrared data [a,b] in the 4000–1200 $cm^{-1}$ region

| Compound $\nu$(N–H) [c] | $\nu$(N–H) [c] | $\nu$(N–H) [d] | $\nu_a$(C=O [e]) | $\nu_a$(COO) | $\nu_s$(COO) | $\Delta\nu$ |
|---|---|---|---|---|---|---|
| $NH_2CONHCH_2CH_2COOH$ | 3434m,<br>3287m | 3266s | 1682s | 1583s | 1303s | 280 |
| $Ph_3SnOCOCH_2CH_2NHCONH_2$ | 3498m<br>(3478m) | 3360m<br>(3489m) | 1618s | 1587s | 1307s | 280 |
| $(^nBu)_3SnOCOCH_2CH_2NHCONH_2$ | 3398m<br>(3397m) | 3327m<br>(3445m) | 1656s | 1569s | 1342s | 227 |
| $(^cC_6H_{11})_3SnOCOCH_2CH_2NHCONH_2$ | 3519m<br>(3512m) | 3374m<br>(3488m) | 1656s | 1586s | 1306s | 280 |
| $(p\text{-tolyl})_3SnOCOCH_2CH_2NHCONH_2$ | 3474m<br>(3488m) | 3359m<br>(3470m) | 1632s | 1582s | 1308s | 274 |
| $Ph_2(^nBu)SnOCOCH_2CH_2NHCONH_2$ | 3466m<br>(3469m) | 3316m<br>(3430m) | 1623m | 1592m | 1307s | 285 |
| $Ph_2(p\text{-ClPh})SnOCOCH_2CH_2NHCONH_2$ | 3455m<br>(3400m) | 3312m<br>(3440m) | 1617s | 1573s | 1271s | 302 |
| $Ph_2(^cC_5H_9)SnOCOCH_2CH_2NHCONH_2$ | 3494s<br>(3478m) | 3365s<br>(3500m) | 1621s | 1590s | 1307s | 283 |

[a] Recorded as Nujol mulls on KBr plates. Values given in parentheses are for $CHCl_3$ solutions of the compounds using a polyethylene cell. [b] s = strong, m = medium. [c] N–H asymmetric stretching of primary amide fragment. [d] N–H asymmetric stretching of the secondary amide fragment. [e] Amido carbonyl asymmetric stretching.

Table 4

Data collection and processing parameters

| | | | | |
|---|---|---|---|---|
| Molecular formula | $C_{22}H_{22}N_2O_3Sn$ | | | |
| Molecular weight | 481.15 | | | |
| Unit cell parameters | $a$ | 11.150(1) Å | $\beta$ | 94.05(1)° |
| | $b$ | 12.719(3) Å | $V$ | 2145.1(6) $Å^3$ |
| | $c$ | 15.164(2) Å | $Z$ | 4 |
| | $F(000)$ | 968 | | |
| Density (calcd.) | 1.490 g $cm^{-3}$ | | | |
| Space group | $P2_1/n$ (non standard No. 14) | | | |
| Standard reflections | (305), (216) | | | |
| $R_{int}$ (from merging of equivalent reflections) | 0.014 | | | |
| Absorption coefficient | 12.14 $cm^{-1}$ | | | |
| Crystal size | 0.32 × 0.34 × 0.40 $mm^3$ | | | |
| Mean $\mu_r$ | 0.214 | | | |
| Transmission factors | 0.500 to 0.567 | | | |
| Scan type and rate | $\omega$; 3.01–15.63 deg $min^{-1}$ | | | |
| Scan range | 0.60° below $K_{\alpha_1}$ to 0.70° above $K_{\alpha_2}$ | | | |
| Background counting | stationary counts for one-fifth of scan time at each end of scan range | | | |
| Collection range | $h, k, +l$; $2\theta_{max} = 55°$ | | | |
| Unique data measured | 4912 | | | |
| Obs. data with $\|F_o\| > 6\sigma(\|F_o\|), n$ | 3355 | | | |
| No. of variables, $p$ | 253 | | | |
| $R_F = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$ | 0.028 | | | |
| Weighting scheme | $w = [\sigma^2(F_o) + 0.0003\|F_o{}^2\|]^{-1}$ | | | |
| $R_G = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$ | 0.035 | | | |
| $S = [\Sigma w(\|F_o\| - \|F_c\|)^2/(n-p)]^{1/2}$ | 1.198 | | | |
| Residual extrema in final difference map | +0.25 to −0.30 e$Å^{-3}$ | | | |

Table 5

Atomic coordinates ($\times 10^5$ for Sn; $\times 10^4$ for other atoms) and equivalent isotropic temperature factors ($\text{Å}^2 \times 10^4$ for Sn and O; $\times 10^3$ for other atoms)

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ [a] |
|---|---|---|---|---|
| Sn(1) | 25100(2) | 19965(2) | 11505(1) | 469(1) |
| O(1) | 1770(2) | 2445(2) | −137(1) | 600(9) |
| O(2) | 1589(2) | 4174(2) | 61(2) | 602(9) |
| O(3) | −1473(2) | 3643(2) | −2547(2) | 630(9) |
| N(1) | −599(3) | 4583(2) | −1424(2) | 52(1) |
| N(2) | −2648(3) | 4506(3) | −1616(2) | 65(1) |
| C(1) | 1043(3) | 2430(3) | 1893(2) | 49(1) |
| C(2) | −115(4) | 2115(4) | 1639(3) | 86(2) |
| C(3) | −1072(4) | 2387(5) | 2129(3) | 103(2) |
| C(4) | −885(4) | 2980(3) | 2866(3) | 73(2) |
| C(5) | 240(4) | 3315(3) | 3120(3) | 71(2) |
| C(6) | 1194(3) | 3035(3) | 2637(3) | 63(1) |
| C(7) | 4064(3) | 2961(3) | 1117(2) | 49(1) |
| C(8) | 4632(3) | 3373(3) | 1870(3) | 71(1) |
| C(9) | 5640(5) | 4007(4) | 1815(4) | 108(2) |
| C(10) | 6076(5) | 4197(5) | 1007(6) | 128(3) |
| C(11) | 5528(5) | 3778(5) | 264(5) | 115(3) |
| C(12) | 4525(4) | 3179(3) | 308(3) | 74(2) |
| C(13) | 2484(3) | 435(3) | 657(2) | 58(1) |
| C(14) | 3256(4) | 105(4) | 48(3) | 82(2) |
| C(15) | 3226(5) | −907(5) | −313(4) | 100(2) |
| C(16) | 2410(6) | −1594(4) | −22(4) | 107(3) |
| C(17) | 1619(6) | −1294(4) | 563(4) | 104(2) |
| C(18) | 1657(5) | −293(3) | 917(3) | 81(2) |
| C(19) | 1535(3) | 3389(3) | −407(2) | 46(1) |
| C(20) | 1220(3) | 3456(3) | −1388(2) | 56(1) |
| C(21) | 606(3) | 4462(3) | −1710(2) | 55(1) |
| C(22) | −1570(3) | 4222(3) | −1887(2) | 46(1) |

[a] $U_{eq}$ defined as one third of the trace of the orthogonalized $U$ tensor.

### *X-Ray analysis*

Diffraction measurements on the title compound were carried out on a Nicolet *R*3*m* four-circle diffractometer (graphite-monochromatized Mo-$K_\alpha$ radiation, $\lambda$ 0.71069 Å). The crystal class, orientation matrix, and accurate unit-cell parameters were determined by standard procedures [11]. The intensities were corrected for absorption using $\psi$-scan data for 12 selected strong reflections [12]. The structure was solved by the heavy-atom method and refined by full-matrix least-squares with anisotropic temperature factors for all non-H atoms. The H-atoms were placed in calculated positions, assigned isotropic temperature factors (0.08 $\text{Å}^2$ for N–H and 0.1 $\text{Å}^2$ for C–H) and included in structure-factor calculations for least-squares refinement. Structure solution and subsequent calculations were performed on a DEC MicroVAX-II computer with the SHELXTL-PLUS system [13]. Analytic expressions of neutral-atom scattering factors incorporating the real and imaginary components of anomalous dispersion were employed [14]. The residuals of the final least-squares cycle and other parameters are listed in Table 4, and the atomic parameters in Table 5. Selected bond distances and angles are listed in Table 6. Lists of hydrogen atom coordinates anisotropic thermal parameters, and structure

Table 6

Selected bond lengths (Å) and bond angles (°) [a]

| | | | |
|---|---|---|---|
| *(i) Coordination geometry about Sn atom* | | | |
| Sn(1)-O(1) | 2.143(2) | Sn(1)-C(1) | 2.123(3) |
| Sn(1)-C(70 | 2.126(3) | Sn(1)-C(13) | 2.122(4) |
| Sn(1)-O(3a) | 2.352(2) | | |
| O(1)-Sn(1)-C(1) | 98.8(1) | O(1)-Sn(1)-C(7) | 95.0(1) |
| C(1)-Sn(1)-C(7) | 121.5(1) | O(1)-Sn(1)-C(13) | 86.2(1) |
| C(1)-Sn(1)-C(13) | 116.0(1) | C(7)-Sn(1)-C(13) | 121.5(1) |
| O(1)-Sn(1)-O(3a) | 171.5(1) | C(1)-Sn(1)-O(3a) | 89.3(1) |
| C(7)-Sn(1)-O(3a) | 82.8(1) | C(13)-Sn(1)-O(3a) | 88.0(1) |
| *(ii) 3-Ureidopropionate ligand* | | | |
| O(1)-C(19) | 1.289(4) | O(2)-C(19) | 1.224(4) |
| O(3)-C(22) | 1.253(4) | N(1)-C(21) | 1.449(5) |
| N(1)-C(22) | 1.33094) | N(2)-C(22) | 1.347(4) |
| C(19)-C(20) | 1.507(4) | C(20)-C(21) | 1.515(5) |
| Sn(1)-O(1)-C(19) | 126.4(2) | C(22)-O(3)-Sn(1b) | 144.1(2) |
| C(21)-N(1)-C(22) | 122.8(3) | O(1)-C(19)-O(2) | 125.1(3) |
| O(1)-C(19)-C(20) | 113.1(3) | O(2)-C(19)-C(20) | 121.7(3) |
| C(19)-C(20)-C(21) | 115.7(3) | N(1)-C(21)-C(20) | 113.6(3) |
| O(3)-C(22)-N(1) | 120.8(3) | O(3)-C(22)-N(2) | 122.0(3) |
| N(1)-C(22)-N(2) | 117.2(3) | | |
| *(iii) Hydrogen bonding* | | | |
| N(1)...O(2c) | 2.882(4) | | |
| C(21)-N(1)...O(2c) | 133.1(3) | C(22)-N(1)...O(2c) | 103.3(3) |
| C(19)-O(2)...N(1c) | 149.0(3) | | |

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[a] Symmetry transformation: a $(1/2+x,\ 1/2-y,\ 1/2+z)$ b $(-1/2+x,\ 1/2-y,\ -1/2+z)$ c $(-x,\ 1-y,\ -z)$.

factors are available from the authors. A drawing, with atom labelling, of the molecular structure of the title compound is shown in Fig. 1, and the molecular packing is shown in Fig. 2.

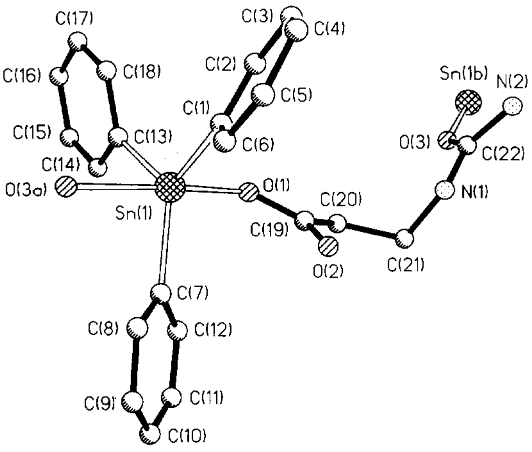

Fig. 1. Molecular geometry and atom numbering of triphenyltin 3-ureidopropionate.

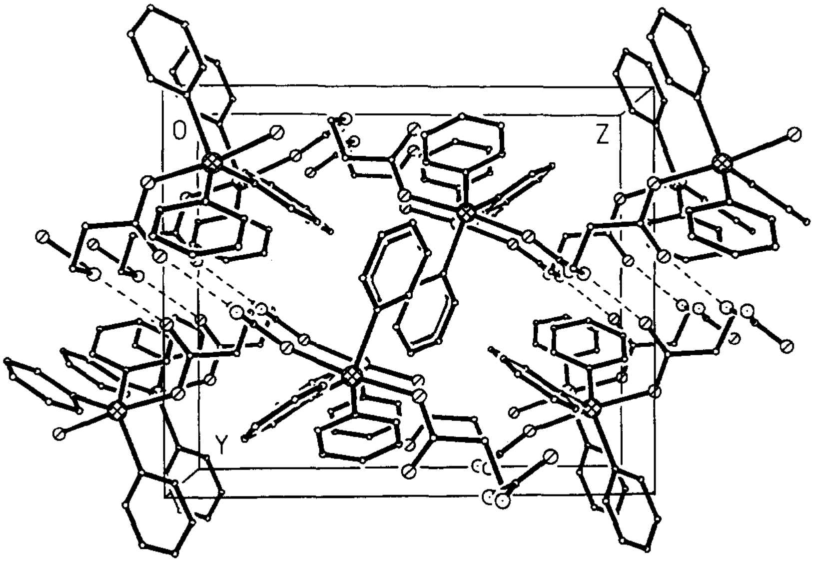

Fig. 2. Perspective view of the molecular packing. The atom types are differentiated by size and shading, and hydrogen bonds are shown as broken lines.

## Results and discussion

The triorganotin 3-ureidopropionates are white crystalline solids with sharp melting points. They yield well-resolved quadrupole split lines in their Mössbauer spectra with little asymmetry in the relative depths of the lines. The isomer shift values for the series of trialkyl-, triphenyl-, and tricycloalkyl-tins and their mixed derivatives are consistent with previously reported Mössbauer data [9,15]. The quadrupole splitting values are directly comparable with those observed for triorganotin levulinates [16], -benzoylbenzoates [17] and -benzoylpropionates [6], and reveal the title compounds to be five-coordinated stannyl esters with *trans*-[$R_3SnX_2$] trigonal bipyramidal geometries at tin [15].

The infrared stretching frequencies of the carboxyl and ureido moieties in the free and complexed ligand are assigned [18,19] as in Table 3. Of interest is the magnitude of the $\nu_{as}(COO) - \nu_{sym}(COO)$ ($\Delta\nu$) separation in the tin-bearing compounds, which exceeds 200 $cm^{-1}$ in each case, indicating a monodentate bonding mode for the carboxylate moiety [20]. For a bridging or chelating carboxylate group, $\Delta\nu \leqslant 150$ $cm^{-1}$ [21], as widely observed in the infrared spectra of triorganotin carboxylates [16]. This prompts consideration of the ureido group as the source of additional attachment to tin to achieve five-fold coordination. The amido nitrogens are less likely to be donors to tin than the amido oxygen because of their lower basicity, and this is supported spectroscopic and structural data on triorganotin adducts of amides [22–24]. The N–H stretching frequencies associated with the primary amide fragment in the compounds are practically unshifted from the value for the free ligand; this is not the case, however, for the N–H stretching frequencies associated with the secondary amide fragment, which are about 46–108 $cm^{-1}$ higher in the compounds. The latter values are further shifted by 100–120 $cm^{-1}$ to higher wavenumbers upon going from solid to solution states. We interpret these features in terms of hydrogen-bonding interactions in the crystals of the compounds, involving N–H and (presumably) an oxygen of the carboxylate group. The amido carbonyl stretching frequency which occurs at 1682 $cm^{-1}$ in the free ligand is shifted to lower wavenumbers ($\Delta\nu$ in the range 26–65 $cm^{-1}$) in the title compounds, and this is taken as evidence for coordinative attachment of this group to tin. It may also be inferred that this coordination is more likely to be inter- than intra-molecular since the latter would imply an 8-membered chelate ring of doubtful stability.

Taken together, the Mössbauer and infrared data indicate that the compounds are ureido-carbonyl bridged polymers with the most electronegative *trans*-$O_2SnC_3$ axially in trigonal bipyramidal geometries about the tin atoms, with some reinforcement of the associated lattice as a result of intermolecular hydrogen bonding interactions between –NH and presumably C(O)O. This conclusion was confirmed by the X-ray structure of triphenyltin 3-ureidopropionate, shown in Figs. 1 and 2. The tin is five-coordinate, with the axial positions of the trigonal bipyramid being occupied by the ester oxygen O(1) and the ureido oxygen O(3a) of an adjacent symmetry-related molecule at the other end. In line with this, the C–O bond distances in the carboxylate group are readily distinguishable: C–O(1) 1.289(4) and C=O 1.224(4) Å, as they are, for example, also in triphenyltin 8-quinolyloxyacetate hydrate (1.278(12) and 1.221(13) Å [5]). The amido C=O bond distance in the ureido fragment is 1.253(4) Å. In contrast, in the carboxylate-bridged triphenyltin 3-benzoylpropionate, the carboxylate C–O bond lengths are nearly equal at 1.263(1) and 1.250(1) Å [6]. The sum of the carbon–tin–carbon angles in the trigonal plane of the title compound is 359.0(1)°. The three phenyl groups are tilted at 15.63, 127.17 and 145.12° with respect to this plane. The apical angle subtended at tin is 171.5(1)°. The tin–oxygen distances are Sn–O(1) 2.143(2) and Sn–O(3a) 2.352(2) Å, and are well within the range usually observed for triorganotin carboxylates; the tin atom is displaced by 0.125 Å in the direction of O(1). In contrast to the Sn–O–C angle of 126.4(2)°, the Sn–O′–C′ angle (primed atom O′ refers to the bridging oxygen atom) is opened up to 144.1(2)° to accommodate the bulk of the ureido moiety. Relatively large Sn–O′–C′ angles, for example, are also found in $Me_3SnOCOCF_3$ (147.0° [25]), $^nBu_3SnOCOCH_2SC(S)NMePh$ (142.6° [7]), $Ph_3SnOCOCH_3$ (142.7° [26]) and $Ph_3SnOCOC_6H_4$-2-Cl (146.4° [27]).

Inspection of the molecular packing of the compound shows that the polymer units are held together in the lattice by relatively strong hydrogen bonding interactions between the amide hydrogen [N(1)–H] and the carboxylate carbonyl oxygen [O(2c)] of an adjacent molecule. The N(1)–O(2c) distance is 2.882(4) Å, which is less than the sum of the van der Waals' radii of 3.11 Å [28]. The distance between the hydrogen-bonded atoms is comparable with that reported in tricyclohexyltin 3-indolylacetate (2.891 Å [29]) and trimethyltin glycinate (2.74 Å [13]). The participation of the carboxyl oxygen in hydrogen-bonding clearly makes possible the formation of Sn–O bridges through the ureido oxygen in the compound; the observed structure provides the first reported example of such an arrangement in a triorganotin carboxylate structure.

## Acknowledgements

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