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# CRYSTAL AND MOLECULAR STRUCTURE OF 1-AZA-5-STANNA-5-CHLOROTRICYCLO[3.3.3.$0^{1,5}$]UNDECANE, A 2,8,9-TRICARBASTANNATRANE

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## Summary

1-Aza-5-stanna-5-chlorotricyclo[3.3.3.$0^{1,5}$]undecane crystallizes in the space group $P6_3$. The unit cell, with $a$ 8.435(3), $c$ 9.243(2) Å, $V$ 569.5(3) Å$^3$, contains two molecules. The structure was refined to a final $R$ value of 0.057. The molecules $ClSn(CH_2CH_2CH_2)_3N$ belong to the point group 3, and the Sn, Cl and N atoms lie on the crystallographic 3-axis. The tin atom has a trigonal bipyramidal environment with the nitrogen and chlorine atoms in apical positions. The tin–nitrogen intramolecular interaction is 2.372(29) Å.

## Introduction

Metallatranes of various elements have been intensively studied in the last twenty years [1]. Because of their unusual cage structure they can be used for systematic studies of transannular donor–acceptor interactions. On the other hand they can also be regarded as models for intermediates along the coordinate for an $S_N2$ reaction. The most studied compounds are the silatranes [2–4], but structural information is also available for derivatives of Ge [5], B [1,6], Al [6] and P [6,7]. In our studies of pentacoordinate organotin compunds [8] we have investigated several stannatranes of the types $RSn(XCH_2CH_2)_3N$ (R = Me, *o*-tolyl, t-Bu; X = O, S, NME) and $RSn(XCOCH_2)_3N$ (R = Me, t-Bu; X = O, NMe). Following NMR measurements the transannular tin–nitrogen interaction was confirmed by X-ray studies for $MeSn(SCH_2CH_2)_3N$ and $t\text{-}BuSn(OCH_2CH_2)_3N$ [9]. A complicated trimeric structure was found for $MeSn(OCH_2CH_2)_3N$ [10]. We recently reported [11] the synthesis of $RSn(CH_2CH_2CH_2)_3N$ (R = Me, Cl), the first being 1-aza-5-

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boratricyclo[3.3.3.0$^{1,5}$]undecane [12], which is only the second reported 2,8,9-tricarbametallatrane. As a start on systematic studies of this type of compound we describe below the molecular structure of the chloro-substituted derivative $ClSn(CH_2CH_2CH_2)_3N$.

## Experimental

The synthesis of $ClSn(CH_2CH_2CH_2)_3N$ has been described elsewhere [11]. Crystals suitable for X-ray analysis were obtained from a concentrated soulution in pyridine. The unit-cell parameters were found by least-squares refinement from the setting angles of 15 reflections: to be $a = b = 8.435(3)$ Å, $c = 9.243(2)$ Å, $Z = 2$, $D_{calc} = 1.72$, $F(000) = 292$.

The symmetry of Weissenberg photographs and systematic absences indicated two possible space groups, $P6_3$ and $P6_3/m$. Because of the lower multiplicity $P6_3$ was selected, and successful analysis confirmed this choice. Intensities of reflections were collected in the $\omega$-scan mode (width 2.0°) with a Syntex $P2_1$ diffractometer, using monochromatic Mo-$K_\alpha$ radiation (0.71069 Å) to a $2\theta$ maximum of 60°. 587 independent intensities were measured, of which 512 were considered as observed ($I > 2.5\sigma(I)$). No absorption or extinction corrections were made ($\mu$ 22.47 $cm^{-1}$). The structure was solved by Patterson and Fourier methods. H-atoms were placed in calculated positions. The full-matrix least-squares refinement of positional and thermal anisotropic parameters of non H-atoms was carried out by the SHELX 76 program and the atom scattering factors were those included in that program. The weighting scheme was $[\sigma^2(F) + 0.0074F]^{-1}$. The final $R$ index is 0.052 for the set of observed reflections, $R$ index is 0.057 for all the reflections *. The final atomic coordinates are listed in Table 1, and the atom numbering is shown in Fig. 1. Tables of observed and calculated structure factors may be obtained from J.M.P.

TABLE 1

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) AND $B_{eq}$ VALUES

| | $x$ | $y$ | $z$ | $B_{eq.}$ |
|---|---|---|---|---|
| Sn(1) | 6667(0) | 3333(0) | 2827(7) | 2.86 |
| Cl(1) | 6667(0) | 3333(0) | 0(0) | 2.62 |
| N(1) | 6667(0) | 3333(0) | 5393(29) | 2.20 |
| C(1) | 3792(11) | 1412(13) | 3215(14) | 3.46 |
| C(2) | 3371(11) | 1721(12) | 4773(18) | 3.80 |
| C(3) | 4862(10) | 1853(12) | 5820(14) | 3.01 |
| H(1) | 3538 | 44 | 3084 | 3.95 |
| H(2) | 2978 | 1681 | 2465 | 3.95 |
| H(3) | 3294 | 2954 | 4826 | 3.95 |
| H(4) | 2054 | 562 | 5082 | 3.95 |
| H(5) | 4881 | 580 | 5785 | 3.95 |
| H(6) | 4549 | 2087 | 6898 | 3.95 |

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* Because $P6_3$ is chiral space group refinement was also carried out for the other enantiomer, but there was no significant difference and so it was not possible to decide between the enantiomers.

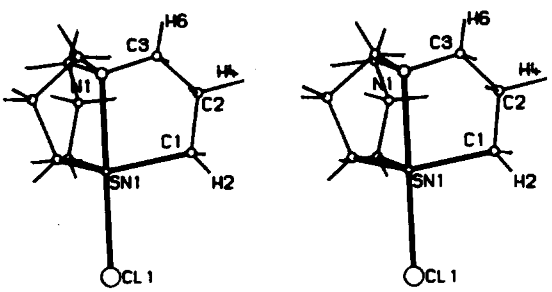

Fig. 1. Stereoscopic view of the molecular structure with atom numbering.

## Results and discussion

The molecular structure is illustrated in Fig. 1. Bond lengths and bond angles are summarized in Table 2. The molecule is symmetric with the chlorine, tin and nitrogen atoms lying on a crystallographic three-fold axis. The Sn–N interaction is weaker than in t-butylstannatrane but stronger than in 5-methyl-2,8,9-trithiostannatrane (Table 3) [9]. The Sn–N distance in $ClSn(CH_2CH_2CH_2)_3N$ is shorter than those in other triorganotin halide complexes involving an intra- or inter-molecular tin–nitrogen interaction [13–15a], although the tin atoms in the latter should have a similar Lewis acidity. This reveals the contribution of the atrane frame to the reduction of the Sn–N bond distance. Because of the short Sn–N interaction the Sn–Cl bond shows the expected lengthening, and is the largest ever produced by a Sn–N complexation [15a,b,–17]. This Sn–Cl bond is longer than those in several pentacoordinated triorganotin chlorides [18–22], shorter than one of the Sn–Cl bonds in $[Bu_3SnCl_2]^-$ [23] and $[Me_3SnCl_2]^-$ [24] and the same as that in $(Ph_2ClSn)_2CH_2 \cdot HMPA$ [25].

The tin–carbon distance can be compared with the equatorial Sn–C bond lengths in $Me_2Sn(SCH_2CH_2)_2NMe$ [15,26] and $Me_3SnCl \cdot HMPA$ [21]; it is shorter than

TABLE 2

BOND DISTANCES (Å) AND BOND ANGLES (°) WITH STANDARD DEVIATIONS

| | |
|---|---|
| Sn(1)-Cl(1) | 2.613(7) |
| Sn(1)-N(1) | 2.372(29) |
| Sn(1)-C(1) | 2.169(8) |
| N(1)-C(3) | 1.460(12) |
| C(1)-C(2) | 1.536(15) |
| C(2)-C(3) | 1.547(14) |
| N(1)-Sn(1)-Cl(1) | 180.0(0) |
| C(1)-Sn(1)-Cl(1) | 99.5(3) |
| C(1)-Sn(1)-N(1) | 80.5(3) |
| C(1)-Sn(1)-C(1) | 117.3(3) |
| C(3)-N(1)-Sn(1) | 105.7(1.3) |
| C(2)-C(1)-Sn(1) | 107.2(5) |
| C(3)-C(2)-C(1) | 110.5(6) |
| C(2)-C(3)-N(1) | 110.8(1.2) |
| C(3)-N(1)-C(3) | 113.0(1.2) |

TABLE 3

SELECTED GEOMETRICAL PARAMETERS OF KNOWN STANNATRANES

| R | X | *d*(Sn–N) (Å) | ΔSn (Å) [a] | ΔN (Å) [b] | XSnX (°) | XSnN (°) | SnNC (°) |
|---|---|---|---|---|---|---|---|
| t-Bu | O | 2.324 | 0.373 | 0.297 | 116.6 | 79.3 | 101.6 |
| Cl | $CH_2$ | 2.372 | 0.359 | 0.395 | 117.3 | 80.5 | 105.7 |
| Me | S | 2.432 | 0.383 | 0.472 | 117.8 [c] | 80.9 | 107.8 |

[a] Deviation of the tin atom from the plane defined by the three oxygen, carbon or sulphur atoms, respectively. [b] Deviation of the nitrogen atom from the plane defined by the three adjacent carbon atoms. [c] Average of the values 117.4, 116.7, and 118.8°.

that in $[Bu_3SnCl_2]^-$ but longer than that in $[Me_3SnCl_2]^-$ [23,24]. The tin atom has a distorted trigonal bipyramidal configuration, with the C(1)–Sn(1)–C(1) bond angle of 117.3° differing slightly from the ideal value of 120°, so that the tin atom lies 0.36 Å below the plane defined by the three equivalent carbon atoms C(1), C(1)★, and C(1)★★ (symmetry elements: ★ $-y,\ x-y,\ z$; ★★ $-x+y,\ -x\ z$). Similar values have been observed for other stannatranes (Table 3), and in 1-azabicyclo[3.3.3]undecane hydrochloride the methine carbon deviates by 0.387 Å from the plane of the three adjacent carbon atoms [27].

As a result of both the Sn–N interaction and the atrane frame the angles around the nitrogen (C(3)–N(1)–C(3), Sn(1)–N(1)–C(3)) differ from the tetrahedral. The nitrogen atom lies 0.395 Å below the plane defined by the three adjacent carbon atoms. This value is intermediate between those found for t-$BuSn(OCH_2CH_2)_3N$ and $MeSn(SCH_2CH_2)_3N$ (Table 3), and comparable with the corresponding angle in $FSi(OCH_2CH_2)_3N$ [4]. In $H_3BP(OCH_2CH_2)_3N$ [7] there is a nearly planar nitrogen atom, whereas in $HC(CH_2CH_2CH_2)_3N \cdot HCl$ the nitrogen atom lies 0.326 above the plane of the three adjacent carbon atoms [27]. These compounds can be regarded as models for the nitrogen inversion pathway. In this connection it would be of interest to investigate this pathway for $RSn(CH_2CH_2CH_2)_3N$ upon variation of R. The torsion angles listed in Table 4 show that the eight-membered rings have a boat-chair conformation, such conformations have been found in other metallatranes [4,9] in 1-azabicyclo[3.3.3]undecane hydrochloride [27], and several stannaocanes [15,26,28,29].

TABLE 4

TORSION ANGLES IN THE EIGHT-MEMBERED RING (°)

| | |
|---|---|
| C(1)★–Sn(1)–C(1)–C(2) | −54.5 |
| Sn(1)–C(1)–C(2)–C(3) | −46.3 |
| C(1)–C(2)–C(3)–N(1) | +58.1 |
| C(2)–C(3)–N(1)–C(3)★ | +78.4 |
| C(3)–N(1)–C(3)★–C(2)★ | −151.8 |
| N(1)–C(3)★–C(2)★–C(1)★ | +58.1 |
| C(3)★–C(2)★–C(1)★–Sn(1) | −46.3 |
| C(2)★–C(1)★–Sn(1)–C(1) | +93.5 |

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