APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2005; **19**: 356–359

DOI:10.1002/aoc.822

Bis[tris(cyclohexyl)tin] azide hydroxide, $(Cy_3Sn)_2N_3(OH)$: X-ray structure determination and comparison with analogous compounds

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Received 23 August 2004; Revised 30 August 2004; Accepted 16 September 2004

The structure of bis[tris(cyclohexyl)tin] azide hydroxide, $(Cy_3Sn)_2N_3(OH)$ (1), contains infinite chains of molecules linked by regularly alternating and μ_2 bridging azide and hydroxide groups that create trigonal bipyramidal tin centres. The bridges, with Sn–N 2.436(11) and 2.385(11) Å and Sn–O 2.199(8) and 2.197(8) Å, are relatively symmetrical. This structure is similar to that of catena bis(trimethyltin) azide hydroxide, $(Me_3Sn)_2N_3(OH)$ (2). In the structure of 1, each terminal nitrogen atom of the azide is bonded to a different tin atom (1,3 or α,γ bridge formation). In the structure of 2, however, only one nitrogen atom of each azide is involved in bridging and bonds to two different tin atoms (1,1 or α,α bridge formation). In this case, the remaining terminal nitrogen atoms act as acceptors for O–H· · ·N hydrogen bonds that link the chains to form infinite sheets. It appears then, from these two examples, that in such compounds the size of the organic species bonded to tin can affect the azide bridging mode and also the packing of the polymeric chains Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: tris(cyclohexyl)tin; pseudo-halostannane; azide; crystal structure

INTRODUCTION

Tris(cyclohexyl)tin compounds have attracted much commercial interest, especially in the area of agrochemicals, the best example being tris(cyclohexyl)tin hydroxide, PLICTRAN, a well used and effective acaricide.[1] Owing in part to such use, much study has been made of the syntheses and structures of tris(cyclohexyl)tin compounds in general, as can be readily seen in the Cambridge Structural Database.[2] Our studies on tris(cyclohexyl)tin compounds stem from an interest in the effect of the bulk of organic groups in triorganotin halides and pseudohalides on coordination at the tin centre.[3,4] In the course of our studies we encountered bis[tris(cyclohexyl)tin] azide hydroxide, $(Cy_3Sn)_2N_3(OH)$ (**1**), as the wholly unexpected product of the attempted recrystallization of tris(cyclohexyl)tin azide, Cy_3SnN_3, from ethanol. The characterization of **1** rests entirely upon the X-ray structure analysis reported here. The tendency for triorganotin azides to undergo partial hydrolysis has been noted previously,[5,6] as in the formation of trimethyltin azide hydroxide, $(Me_3Sn)_2N_3(OH)$ (**2**), from the parent trimethyltin azide, Me_3SnN_3 (**3**). It is of some interest to compare the structure of **1** with those of **2** and **3** and other related compounds in terms of Sn–O and Sn–N bond lengths and the presence or absence of bridging.

RESULTS AND DISCUSSION

The asymmetric unit of **1** is shown in Fig. 1, and selected bond lengths and angles are given in Table 1. It occurs, Fig. 2, in the form of zig-zag polymeric chains propagated in the direction of *a* in which μ_2 bridging azide and hydroxyl groups alternate along the length of the chain. This creates trigonal bipyramidal tin centres with the azide and hydroxyl groups axial and equatorial cyclohexyl

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Table 1. Selected bond lengths (Å) and angles (°) for **1**

Sn1–C1	2.172(13)	Sn2–C19	2.170(12)
Sn1–C7	2.124(11)	Sn2–C25	2.137(14)
Sn1–C13	2.177(16)	Sn2–C31	2.158(13)
Sn1–N1	2.436(11)	Sn2–N3	2.385(11)
Sn1–O1	2.199(8)	$Sn2-O1^{i}$	2.197(8)
N1–N2	1.160(14)	N2–N3	1.206(14)
C1–Sn1–C7	122.7(5)	C19–Sn2–C25	125.2(5)
C1–Sn1–C13	119.3(7)	C19–Sn2–C31	110.2(5)
C7–Sn1–C13	115.7(6)	C25–Sn2–C31	123.2(5)
N1–Sn1–C1	86.1(4)	N3–Sn2–C19	84.6(5)
N1–Sn1–C7	84.9(4)	N3–Sn2–C25	85.3(4)
N1–Sn1–C13	83.9(6)	N3–Sn2–C31	88.1(5)
O1–Sn1–C1	92.0(4)	$O1^{i}-Sn2-C19$	95.6(4)
O1–Sn1–C7	97.9(4)	$O1^{i}-Sn2-C25$	93.1(4)
O1–Sn1–C13	95.1(5)	$O1^{i}-Sn2-C31$	93.6(5)
N1–Sn1–O1	177.1(4)	$N3-Sn2-O1^{i}$	178.1(4)
Sn1–N1–N2	123.1(9)	Sn2–N3–N2	127.5(9)
$Sn1-O1-Sn2^{ii}$	140.0(5)	N1–N2–N3	176.7(13)

Symmetry codes: (i) $x - 1/2, 3/2 - y, z$; (ii) $x + 1/2, 3/2 - y, z$.

groups. The hydroxyl groups with Sn–O distances of 2.197(8) and 2.199(8) Å and Sn–O–Sn angle of 140.0(5)° bridge in a symmetrical manner, and the azide groups with Sn–N distances of 2.385(11) and 2.436(11) Å and Sn–N–N angles of 123.1(9) and 127.5(9)° bridge only slightly less symmetrically. All of the cyclohexyl rings are in the chair conformation, with C–C distances and internal C–C–C angles more or less as expected, provided that due allowance is made for the disorder noted in the Experimental section below.

The only close analogues to **1** for which structural data are available in the Cambridge Structural Database[2] are **2**[7] and the corresponding isocyanate hydroxide, $(Me_3Sn)_2(NCO)(OH)$ (**4**).[8] It is possible, however, to compare the situations of the azide and hydroxide ligands in the structure of **1** with those found in a wider range of compounds. As shown in Table 2, in compounds of the form R_3SnN_3 with bulky R [R = 2-methyl-2-phenylpropyl (Neo) and ^{t}Bu],[3,9] azide functions as a monodentate ligand. With less-bulky R, azide fulfils a μ_2 bridging function either in α,α mode (R = Me),[10] where only one terminal nitrogen atom forms the bridging bonds, or in α,γ mode (R = phenyl,[11] benzyl[12]), where both terminal nitrogen atoms are involved. Also notable in Table 2 is the α,α bridging mode of azide in the azide

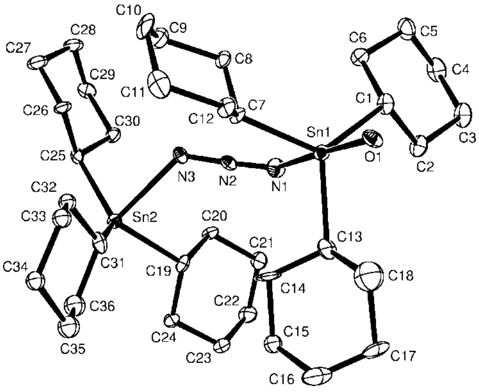

Figure 1. The asymmetric unit of **1**. Non-hydrogen atoms are shown as 20% probability displacement ellipsoids and all hydrogen atoms and the carbon atoms of the B component of the disordered cyclohexyl groups have been omitted for clarity.

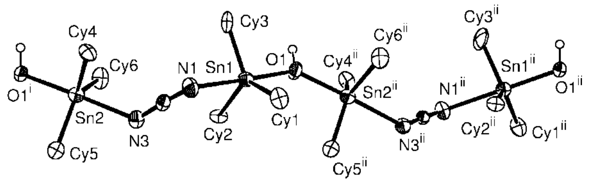

Figure 2. Part of a chain of molecules of **1** propagated in the direction of *a* (left to right across the page). For clarity, cyclohexyl groups are represented by the carbon atoms directly bonded to tin and labelled Cy(*n*). All non-hydrogen atoms shown are represented as 50% probability displacement ellipsoids and hydrogen atoms as spheres of arbitrary radii. Symmetry codes: (i) $x - 1/2, 3/2 - y, z$; (ii) $x + 1/2, 3/2 - y, z$.

Table 2. Comparison of Sn–N and N–N bond lengths (Å) in 4- and 5-coordinate triorganotin azides

	4-coordinate Sn		5-coordinate Sn				
Bond	$^{t}Bu_3SnN_3$ at 293 K Ref. 9	$(Neo)_3SnN_3$ at 150 K Ref. 3	Me_3SnN_3 at RT Ref. 10 $\alpha,\alpha N_3$	$(Me_3Sn)_2N_3(OH)$ at RT Ref. 7 $\alpha,\alpha N_3$	Ph_3SnN_3 at RT Ref. 11 $\alpha,\gamma N_3$	$(PhCH_2)_3SnN_3$ at 293 K Ref. 12 $\alpha,\gamma N_3$	$(Cy_3Sn)_2N_3(OH)$ at 120 K This work $\alpha,\gamma N_3$
$Sn-N_\alpha$	2.101(4)	2.247(4)	2.386(3)	2.439(17)	2.186(3)	2.157(10)	2.385(11)
Sn–N	—[a]	—[a]	2.386(3)	2.613(17)	2.714(4)	2.546(11)	2.436(11)
$N_\alpha-N_\beta$	1.188(7)	—[b]	1.218(9)	1.16(3)	1.194(4)	1.078(13)	1.206(14)
$N_\beta-N_\chi$	1.121(8)	—[b]	1.145(10)	1.20(3)	1.146(4)	1.087(14)	1.160(14)

[a] Monodentate N_3.

[b] Limited refinement renders N–N distances imprecise.

hydroxide **2**, with R = Me, as distinct from the α,γ mode of bridging in **1**, with R = cyclohexyl. This implies that the difference in azide bridging mode between **1** and **2** is brought about, as for the simple azides, by the difference in the bulk of the organic R species, Cy as against Me. It is clear that the bulk of the organic R groups will control the closeness of approach of adjacent tin centres and, thus, determine whether bridging can occur and, if it does, in what mode.

Table 3 shows Sn–O bond lengths in a variety of triorganotin hydroxyl compounds. The trimesityl compound is the only molecular structure and has the shortest Sn–O bond. All of the other compounds shown are linear polymers. In isostructural **2** and **4**, the polymer chains are propagated by regular alternation of pseudohalide (azide in **2** and isocyanate in **4**) and hydroxyl groups. In both cases the pseudohalide groups bridge in α,α mode and the remaining terminal nitrogen atoms of the azides in **2** and the oxygen atoms of the isothiocyanates in **4** act as acceptors for hydrogen bonds, with the hydroxyl groups of adjacent polymer chains as donors. In this way, polymeric sheets are produced (Fig. 3). In contrast, in **1** there is no hydrogen bonding between the polymer chains. Indeed, there are only van der Waals interactions between neighbouring chains. The small bulk of the organic groups, methyl in both **2** and **4**, is also implicated here, because, in these cases, it allows the chains to pack together closely enough for hydrogen bonding to take place.

CONCLUSIONS

The structure of bis[tris(cyclohexyl)tin] azide hydroxide (**1**), as determined by X-ray crystallography, is shown to be that of a linear polymer with regularly alternating μ_2 azide and hydroxyl groups. Comparison with a number of other triorganotin azides and hydroxides suggests that the azide bridging mode is dependent upon the the bulkiness of the organic groups attached to tin. The difference between the purely linear polymeric structure of **1** and the two-dimensional polymeric structure of its trimethyl analogue, brought about in the latter by the formation of O–H$\cdots$N hydrogen bonds between adjacent chains, is likewise attributed to the difference in size of the organic groups attached to tin.

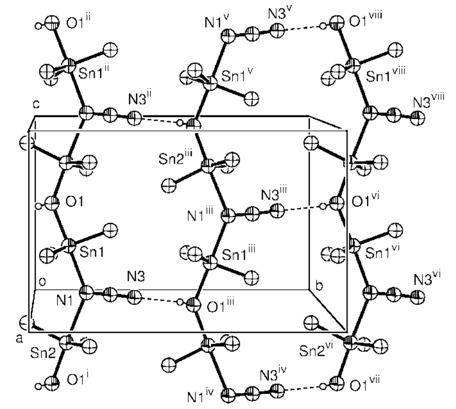

Figure 3. A layer of molecules of $(Me_3Sn)_2N_3(OH)$ (**2**). The layer is parallel to (100) and centred on $x = 1/4$. Dashed lines indicate the O–H$\cdots$N hydrogen bonds. Symmetry codes: (i) $x, y, z-1$; (ii) $x, y, z+1$; (iii) $1/2-x, 1/2+y, 1/2-z$; (iv) $1/2-x, 1/2+y, -z-1/2$; (v) $1/2-x, 1/2+y, 3/2-z$; (vi) $x, y+1, z$; (vii) $x, y+1, z-1$; (viii) $x, y+1, z+1$.

EXPERIMENTAL

Preparation of tris(cyclohexyl)tin azide, Cy_3SnN_3, and growth of crystals of 1

A solution of $(Cy)_3SnCl$ (2 mmol) in Me_2CO (15 ml) and a suspension of NaN_3 (5 mmol) in Me_2CO (15 ml) were mixed. After stirring at room temperature overnight, the reaction mixture was filtered. The filtrate was shaken with a further suspension of NaN_3 (5 mmol) in Me_2CO (15 ml) for 4 h, all volatiles removed by rotary evaporation and the residue extracted into $CHCl_3$. The chloroform extract was dried and rotary evaporated to leave a solid residue.

Crystallization of this residue from EtOH gave bis[tris(cyclohexyl)tin] azide hydroxide, $(Cy_3Sn)_2N_3(OH)$ (**1**), as determined by X-ray crystallography. M.p. 133–136 °C.

X-ray crystallography

Intensity data were collected at 120(2) K, by means of the Enraf Nonius KappaCCD area detector diffractometer of the EPSRC's crystallography service at Southampton, for a colourless crystal, $0.20 \times 0.30 \times 0.35\ mm^3$, with Mo K$\alpha$ radiation, $\lambda = 0.71073$ Å so that $\theta_{max} = 27.5°$. The entire process of data collection, cell refinement and data reduction was accomplished by means of the programs DENZO[16]

Table 3. Comparison of Sn–O bond lengths (Å) in 4- and 5-coordinate triorganotin hydroxyl compounds

Bond	4-coordinate Sn	5-coordinate Sn				
	$(Mesityl)_3SnOH$ at RT Ref. 13	$[Ph_3SnOH]_n$ at RT Ref. 14	$[Et_3SnOH]_n$ at RT Ref. 15	$(Cy_3Sn)_2N_3(OH)$ at 150 K This work	$(Me_3Sn)_2N_3(OH)$ at RT Ref. 7	$(Me_3Sn)_2(NCO)(OH)$ at RT Ref. 8
Sn–O	1.999(6)	2.197(5)	2.155(5)	2.197(8)	2.093(13)	2.14(5)
Sn–O	—	2.255(5)	2.244(5)	2.199(8)	2.211(13)	2.15(5)

and COLLECT.[17] Correction for absorption by a semi-empirical method based upon the variation in intensity of equivalent reflections was achieved with the program SORTAV.[18,19] The initial structure solution was obtained by the heavy-atom technique with the program SHELXS-86[20] and completed and refined by full-matrix least squares on F^2 with SHELXL-97.[21] In order to accommodate disorder in two of the cyclohexyl groups, one associated with each of the two tin atoms, atoms C(15), C(18) and C(32–36) were split into pairs as, for example, C(15A)/C(15B), with the atoms of each pair now in sites with occupancy factors of 0.5 and refined with isotropic displacement parameters and with restraints applied to the C–C distances and internal C–C–C angles of the disordered rings. Anisotropic thermal vibration parameters were refined for all other non-hydrogen atoms. In the final stages of refinement, hydrogen atoms were introduced in calculated positions, taking full account of the disorder noted above, and refined with a riding model. The program ORTEP-3 for Windows[22] was used in the preparation of the figures, and SHELXL-97 and PLATON[23] were used for bond lengths and angles and other molecular geometry calculations. PLATON was used, in particular, for calculations based upon crystallographic data extracted from the Cambridge Structural Database.[2]

Crystal data

Formula: $C_{36}H_{67}N_3OSn_2$; $M = 795.31$; orthorhombic, $Pna2_1$, $a = 19.9546(15)$ Å, $b = 17.2336(11)$ Å, $c = 10.9161(6)$ Å, $Z = 4$, $V = 3753.9(4)$ Å^3, 6249 independent reflections ($R_{\mathrm{int}} = 0.050$), 5481 observed reflections [$I > 2\sigma(I)$]; parameters refined: 373; number of restraints: 134; Flack parameter:[24] $-0.03(7)$; $R(F)$: 0.075 (obs. data); $wR(F^2) = 0.178$ (all data); $\Delta\rho_{\max} = 3.42$ e$^-$Å^{-3} (<0.90 Å from tin). CCDC deposition no: 231210.

Acknowledgements

We are indebted to the EPSRC for the use of both the Chemical Database Service at Daresbury, primarily for access to the Cambridge Structural Database, and the X-ray service at the University of Southampton for data collection. We thank CNPq, Brazil, for financial support.

REFERENCES

1. Smith PJ (ed.). *Chemistry of Tin*, second edition. Blackie: Glasgow, 1997.
2. Allen FH. *Acta Crystallogr. Sect. B* 2002; **58**: 380. DOI: 10.1107/S0108768102003890.
3. Bomfim JAS, Filgueiras CAL, Howie RA, Low JN, Skakle JMS, Wardell JL, Wardell SMSV. *Polyhedron* 2002; **21**: 1667. DOI: 10.1016/S0277-5387(02)01030-6.
4. Howie RA, Moura MVH, Wardell JL, Wardell SMSV. *Polyhedron* 2004; **23**: 2331. DOI 10.1016/j.poly.2004.08.001.
5. Thayer JS, West R. *Inorg. Chem.* 1964; **3**: 889.
6. Bertazzi N, Alonzo G, Barbieri R, Herber RH. *J. Organometal. Chem.* 1974; **65**: 23. DOI: 10.1016/S0022-328X(00)83883-8.
7. Allmann R, Hohlfeld R, Olejnik S, Lorberth J. *J. Organometal. Chem.* 1981; **210**: 51. DOI: 10.1016/S0022-328X(00)86644-9.
8. Hall JB, Britton D. *Acta Crystallogr. Sect. B* 1972; **28**: 2133. DOI: 10.1107/S0567740872005667.
9. Hänssgen D, Jansen M, Leben C, Oster T. *J. Organometal. Chem.* 1995; **494**: 223. DOI: 10.1016/0022-328X(95)05420-T.
10. Allmann R, Hohlfeld R, Waskowska A, Lorberth J. *J. Organometal. Chem.* 1980; **192**: 353. DOI: 10.1016/S0022-328X(00)81226-7.
11. Wharf I, Wojtowski R, Bowes C, Lebuis A-M, Onyszchuk M. *Can. J. Chem.* 1998; **76**: 1827.
12. Burke AC, Mahon MF, Molloy KC. *Appl. Organometal. Chem.* 2003; **17**: 735. DOI: 10.1002/aoc.478.
13. Reuter H, Puff H. *J. Organometal. Chem.* 1989; **379**: 223. DOI: 10.1016/0022-328X(89)85162-9.
14. Glidewell C, Liles DC. *Acta Crystallogr. Sect. B* 1978; **34**: 129. DOI: 101107/S0567740878002447.
15. Deacon GB, Lawrentz E, Nelson KT, Tiekink ERT. *Main Group Met. Chem.* 1993; **16**: 265.
16. Otwinowski Z, Minor W. In *Macromolecular Crystallography, part A*. Carter Jr CW, Sweet RM (eds). Methods in Enzymology, vol. 276. Academic Press: New York, 1997; 307–326.
17. Hooft RWW. COLLECT. Nonius BV, Delft, The Netherlands, 1998.
18. Blessing RH. *Acta Crystallogr. Sect. A* 1995; **51**: 33. DOI: 10.1107/S0108767394005726.
19. Blessing RH. *J. Appl. Crystallogr.* 1997; **30**: 421. DOI: 10.1107/S0021889896014628.
20. Sheldrick GM. *Acta Crystallogr. Sect. A* 1990; **46**: 467. DOI: 10.1107/S0108767390000277.
21. Sheldrick GM. SHELXL-97. Program for crystal structure refinement. University of Göttingen, Germany, 1997.
22. Farrugia LJ. *J. Appl. Crystallogr.* 1997; **30**: 565. DOI:10.1107/S0021889897003117.
23. Spek AL. *J. Appl. Crystallogr.* 2003; **36**: 7. DOI: 10.1107/S0021889802022112.
24. Flack HD. *Acta Crystallogr. Sect. A* 1983; **39**: 876. DOI: 10.1107/S0108767383001762.