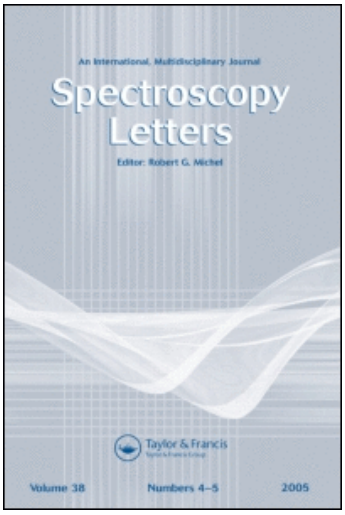

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Structural Investigation of (5-Amino-1,3,4-thiadiazolyl-2-thionato)trimethyltin(IV): 1D Chains Generated by Hydrogen Bonding

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ABSTRACT The geometry of the four-coordinated Sn atom in the title compound, $(CH_3)_3Sn(C_2H_2N_3S_2)$, is distorted tetrahedral with three Sn–C bonds and one Sn–S bond. Two crystallographically distinct molecules **a** and **b** within the asymmetric unit are hydrogen bonded. Intermolecular "N–H···N" hydrogen bond interactions generate infinite 1D chains consisting of alternating, centrosymmetric R2,2(8) and R4,2(10) rings.

KEYWORDS crystal structure, trimethyltin(IV) 5-amino-1,3,4-thiadiazolyl-2-thionate

INTRODUCTION

The heterocyclic thionates are interesting on account of the diversity of the coordination modes that stem from the presence of deprotonated heterocyclic thioamide (–N–C–S–) group. The metal coordination of substituted 1,3,4-thiadiazole has attracted considerable attention in recent years because of its relevance to metal interactions with biological molecules. 5-Amino-3H-1,3,4-thiadiazole-2-thione exhibits thione-thiol tautomerism,[1] and both forms coexist in the solid state, but the thione form is the dominant one in the solid state and the equilibrium shifts to thiol form in solution. 5-Amino-1,3,4-thiadiazole-2-thiol is a versatile ligand because it can coordinate to a metal ion in several ways. At least, four bonding modes between ligand and tin are conceivable (Fig. 1). The coordination with exocyclic sulfur (Fig. 1a) is found in every kind of monomeric structure. However, the coordination with only ring nitrogen (Fig. 1b) is not common for tin compounds, but it is often found in zinc derivatives.[2] The chelation with both the S atoms (Fig. 1c) is to our knowledge unknown, but N, S chelation (Fig. 1d) is commonly observed in organotin(IV) compounds.[3,4] In addition to this, bridging between different molecules via the heterocycles rather than chelation and/or distortion from regular geometry may also be possible. Recently, increasing investigation of organotin(IV) derivatives of heterocyclic thionates[3] such as 2,5-dimercapto-1,3,4-thiadiazole (Bismithol-I)

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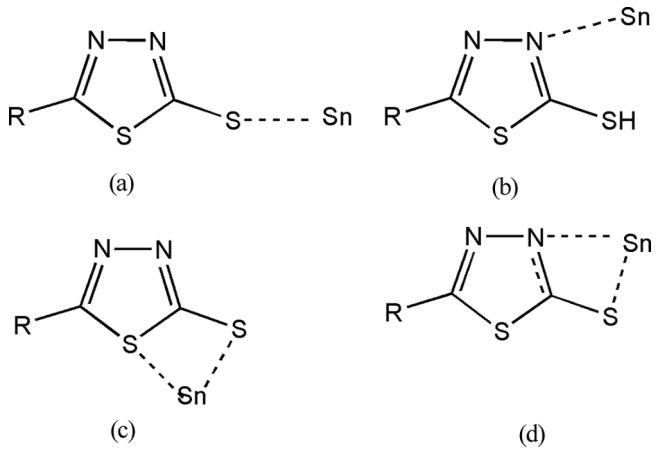


FIGURE 1 **Possible modes of coordination ((a) to (d)) of heterocyclic ring containing thioamide group.**

has occured to learn the nature of their versatile bonding modes in well-defined solid-state crystal structures. The crystal structures of triphenyltin 5-amino-1,3,4-thiadiazolyl-2-thiolate and organotin-(IV) derivatives of 2,5-dimercapto-1,3,4-thiadiazole have been reported.[3,5] It has been revealed from the reported x-ray data that several factors, viz., the spatial geometries of ligand, spatial resistant from R groups bound to tin, and so forth, can influence the topologies of the organotin(IV) derivatives of heterocyclic thionates. In view of this and our continuing interest on the organotin(IV) derivatives of heterocyclic thionates,[6–8] we study and report herein the detailed structural analysis of (5-amino-1,3,4-thiadiazolyl-2-thionato)trimethyltin(IV) on the basis of single crystal x-ray spectral studies along with other previously reported spectroscopic data.

MATERIALS AND METHODS

(5-Amino-1,3,4-thiadiazolyl-2-thionato)trimethyltin (IV) was synthesized according to the previously reported method.[6] The materials used for its preparation are same as reported previously.[6] A methanol solution (10 mL) of trimethyltin(IV) chloride (1.60 g, 8 mmol) was added to the sodium salt of 5-amino-1,3,4-thiadiazole-2-thiol (1.10 g, 8.0 mmol) in methanol (10 mL) and stirred at room temperature for 30–35 h under dry nitrogen atmosphere. From the resulting mixture, the excess of solvent was removed by slow evaporation under vacuum. The solid residue was redissolved in dichloromethane-methanol (2:1, v/v) mixture, and the solvent was allowed to evaporate slowly at room temperature. After 12–15 h, needle-shaped crystals were collected from the concentrated solution by filtration and dried at room temperature.

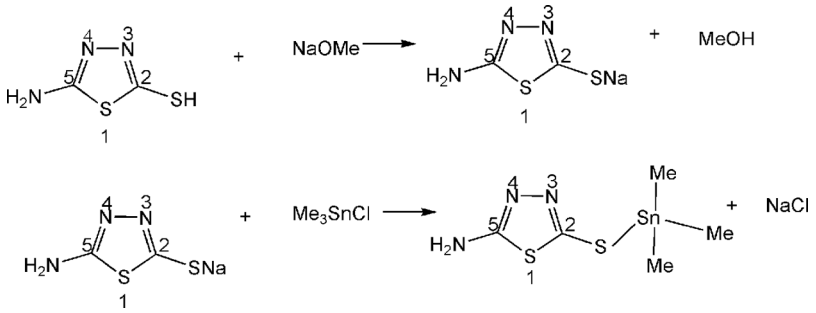
$Me_3Sn(C_2H_2N_3S_2)$: light yellow crystalline solid; m.p. 138–140°C. Yield (%): 75; Analysis Calcd. for $C_5H_{11}N_3S_2Sn$: C, 20.29%; H, 3.74%; N, 14.20%; S, 21.66%; Sn, 40.10%. Found: C, 20.25%; H, 3.68%; N, 14.15%; S, 21.67%; Sn, 40.11%. UV-Vis: $\pi \rightarrow \pi^*$ at λ 209 nm (ε: 2907 L mol^{-1} cm^{-1}); $n \rightarrow \pi^*$ at λ 260 nm (ε: 6726 L mol^{-1} cm^{-1}) (in MeOH); IR/far-IR (cm^{-1}): 3270 br (ν_{as} NH_2), 3066 br (ν_{as} NH_2), 1632 s (ν C=N + δ N–H), 1496 vs, 1410 w (ν C=N/ring mode), 1320 w, 1126 s (δ N–H + ν C=N), 1196 w (ν C=S), 1032 vs (ν N–N), 780 vs (δ N–H + ring-in-plane bending), 678 sh (ring torsion + ν C–S ring + ν C–S exocyclic), 605 m (ν_{as} Sn–C), 537 s (ν_s Sn–C), 426 vs (ν Sn–N), 345 w (ν Sn–S); ^{13}C NMR (in DMSO-d_6 ppm): δ −2.0 (C-α), 172.0 (C–S), 169.1 (C=N); ^{119}Sn NMR (in CD_3OD): δ − 211.20 ppm; ^{119}Sn Mössbauer: Q.S. (mm s^{-1}): 2.58, I.S. (mm s^{-1}): 1.36, ρ(Q.S./I.S.): 1.90, τ (L) 1.90, τ (R) 1.10.[6]

X-ray Crystallographic Measurement

Crystals were mounted in Lindemann capillaries under nitrogen. All x-ray crystallographic data were collected on a Bruker Kappa APEX8 CCD diffractometer with graphite monochromated Mo Ka radiation ($\lambda = 0.71073$ Å) at 298(2) K at Institute Instrumentation Centre (IIC), IIT Roorkee, Roorkee, India. Correction for semiempirical from equivalents was applied. The structure was solved by direct methods and refined by a full-matrix least-squares procedure based on F^2 using the SHELXL-97 program system.[9] All the hydrogen atoms were placed geometrically, and their displacement parameters were refined isotropically on group basis. Molecular geometry was prepared by PLATON,[10] and software used to prepare materials for publication was WinGX publication routines.[11] CCDC reference number 665110 contains the supplementary data for this paper and is available from the CCDC electronic archives.

RESULTS AND DISCUSSION

The reaction of trimethyltin chloride with sodium salt of 5-amino-3H-1,3,4-thiadiazole-2-thione led to the formation of (5-amino-1,3,4-thiadiazolyl-2-thionato)-trimethyltin(IV) (Scheme 1).



SCHEME 1 **Reaction pathway for the formation of $Me_3Sn(C_2H_2N_2S_2)$.**

5-Amino-3H-1,3,4-thiadiazole-2-thione exhibits two characteristic infrared absorption bands at 2622 and 1240 cm^{-1} which have been assigned to the ν(S–H) and ν(C=S), respectively, indicating the coexistence of both thione and thiol forms in the solid state.[6] In 5-(amino-1,3,4-thiadiazolyl-2-thionato)trimethyltin(IV), the ν(S–H) is not observed indicating the deprotonation of thiol form, whereas the ν(C=S) undergoes a downward shift by 44 cm^{-1} indicating the coordination of thiolo sulfur to tin. Further, $\nu(NH_2)$ modes undergo a downward shift by ~77–90 cm^{-1} when compared with the uncoordinated ligand, but a downward shift by 200–300 cm^{-1} would have been required for the coordination of the ligand through the amino group.[6] Therefore, the observed downward shift in $\nu(NH_2)$ is mainly due to its involvement in inter-/intramolecular hydrogen bonding.[6]

Two characteristic N(3)–H stretching modes of thione tautomer of the ligand observed at 3108 and 2923 cm^{-1} are absent in the IR spectrum of $Me_3Sn(C_2H_2N_3S_2)$ indicating the deprotonation of the N(3)–H of the ligand. The combination bands, viz., [δ (N–H) minor + ν(C=N) major], ν(C=N)/ring mode and [δ(N–H) major + ν(C=N) minor] observed at 1604, 1547/1476, and 1365 cm^{-1}, respectively, in the ligand are significantly shifted in $Me_3Sn(C_2H_2N_3S_2)$, indicating that the ring nitrogen N(3) is coordinated to tin. The above mode of coordination of 5-amino-1,3,4-thiadiazolyl-2-thiol through N(3) and exocyclic sulfur is further confirmed by the appearance of two new bands at 426 and 345 cm^{-1}, which are assigned to ν(Sn–N) and ν(Sn–S), respectively.

The observed Q.S. value of 2.58 mm s^{-1} in the ^{119}Sn Mössbauer spectrum of (5-amino-1,3,4-thiadiazolyl-2-thionato)trimethyltin(IV) is substantially lower than those typical for *trans*-trigonal-bipyramidal configuration (Fig. 2a) of tin as found in R_3SnXY fragments (3.0–4.0 mm s^{-1}) of triorganotin carboxylates but slightly higher than those for *cis*-trigonal-bipyramidal (1.70–2.40 mm s^{-1}) (Fig. 2b) and pseudotetrahedral arrangements.[12] Therefore, a highly distorted tetrahedral structure involving a weak interaction between N(3) and Sn or a distorted *cis*-trigonal-bipyramidal structure has been suggested for this complex. The ρ(Q.S./I.S.) value of 1.90 also indicates four coordination number of tin. The high geometric distortion is due to four-membered Sn, S, C, and N chelate ring. However, the observed ^{119}Sn NMR shift (δ −211.20 ppm) in CD_3OD corresponds with five-coordinate trigonal-bipyramidal structure involving one solvent molecule.

The perspective view and cell packing view of (5-amino-1,3,4-thiadiazolyl-2-thionato)trimethyltin (IV) are shown in Figs. 3 and 4, respectively. The crystal data and structure refinement parameters are presented in Table 1. The selected bond lengths/bond angles and H-bonding interactions are given in Tables 2 and 3, respectively. (5-Amino-1,3,4-thiadiazolyl-2-thionato)trimethyltin(IV) contains two crystallographically independent monomers **a** and **b** in an asymmetric unit (Fig. 3). The conformations of these two independent molecules are almost the

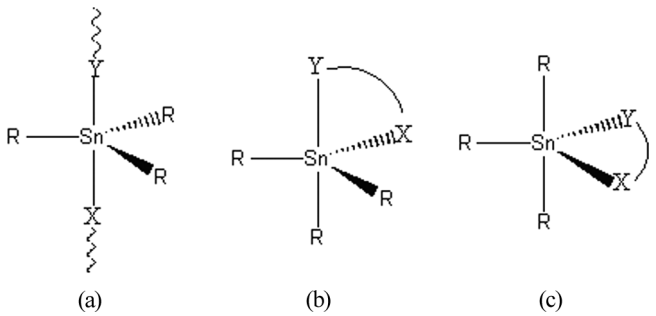


FIGURE 2 **Three possible isomers ((a) to (c)) of R_3SnXY.**

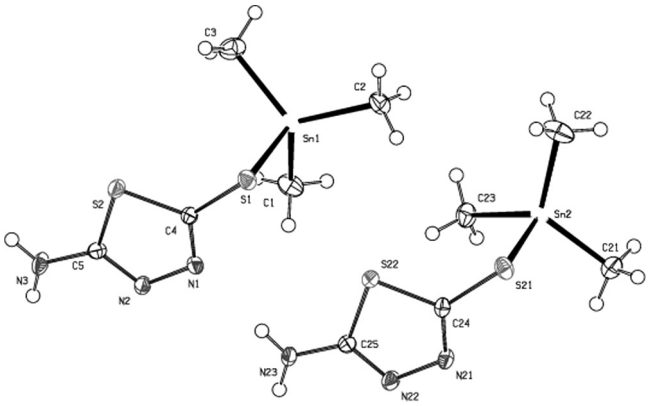


FIGURE 3 **Ortep diagram of asymmetric unit of $Me_3Sn(C_2H_2N_2S_2)$ showing atom-numbering scheme. Ellipsoids drawn at 50% probability level.**

same, only with very small differences in bond lengths and bond angles (see Table 2). The coordination polyhedron around tin in the monomers is defined by three Sn–C (methyl groups) and one Sn–S [$(N–C–S)^-$ group] bonds leading to a distorted tetrahedral environment. The observed Sn–S bond distances of monomers **a** and **b**; Sn(1)–S(1) 2.492(13) Å and Sn(2)–S(21) 2.506(14) Å (Table 2), are similar to those (2.467/2.489 Å) reported for triphenyl-/tribenzyltin(IV)/dibutyltin(IV) derivatives of 2,5-dimercapto-1,3,4-thiadiazole, $(R_3Sn)_2(SC_2SN_2S)$[3]/[*n*-$Bu_2Sn(SC_2SN_2S)]_5$(2.494 Å),[4] and approach the sum of the covalent radii of tin and sulfur (2.42 Å).[13] The observed C–S bonds distances correspond with the C–S single bond,[3,4] which clearly indicates that the ligand offered thiolate species to substitute the chloride anion of trimethyltin(IV) chloride.

In the heterocyclic ring, the observed N(1)–N(2) 1.374 (5) Å and N(21)–N(22) 1.387 (6) Å distances and C–N bond distances [C(4)–N(1) 1.302(6) Å, C(5)–N(2) 1.309(6) Å, C(24)–N(21) 1.296(6) Å and C(25)–N(22) 1.300(6) Å)] (Table 2) are comparable with N–N single-bond and C=N double-bond distances, respectively, reported in the similar types of complexes,[3,4] which further confirm the bonding of the ligand to tin via its thiolate form. The observed C–Sn–C bond angles (Table 2) are slightly larger than the ideal tetrahedral angle indicating the distorted geometry. However, the observed intramolecular Sn–N bond distances, Sn1–N1 3.864 Å and Sn2–N21 3.963 Å are slightly larger than the sum of the van der Waals radii of tin and nitrogen atoms (3.74 Å)[14] and may be considered as very weak secondary interactions, and such interactions may also distort the coordination geometry of the complex. If these interactions are taken into consideration, the other alternative of having highly distorted *cis*-trigonal-bipyramidal geometry cannot be ignored, but N(1)–Sn(1)–C angle has not been observed.

The crystallographically distinct molecules **a** and **b** are tightly hydrogen bonded (Fig. 4). The most interesting feature of this complex is that the four N–H···N bonds form hydrogen-bonded molecular chains in the [001] direction. Graph set analysis of the motifs formed are alternate R2,2(8) and R4,2(10) (Fig. 4). These are fused, centrosymmetric rings formed about centers of symmetry. Interestingly, some intermolecular nonbonding S–S and N–N interactions between monomers **a** and **b** or

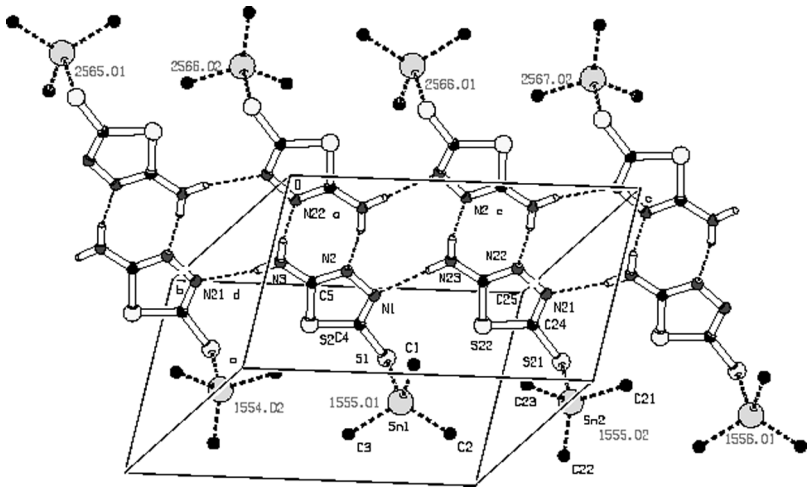


FIGURE 4 **A stereoscopic view of part of the crystal structure of $Me_3Sn(C_2H_2N_2S_2)$ showing the formation of molecular chains along R[001] direction. Hydrogen bonds shown as thin dashed lines show the formation of R2,2(8) and R4,2(10) rings.**

TABLE 1 Crystal Data and Structure Refinement Parameters for $(CH_3)_3Sn(C_2H_2N_3S_2)$

Crystal data	$(CH_3)_3Sn(C_2H_2N_3S_2)$
Empirical formula	$C_5H_{11}N_3S_2Sn$
Formula weight	296.02
Crystal system	triclinic
Space group	*P*1
Unit cell dimensions	
a (Å)	7.6836 (10)
b (Å)	11.4550 (15)
c (Å)	12.2866 (15)
α (°)	104.667 (8)
β (°)	103.219 (8)
γ (°)	91.532 (8)
V (Å^3)	1014.3 (2)
Z	4
Calcd. density (mg m^{-3})	1.938
Absorption coefficient (mm^{-1})	2.878
F (000)	576
Crystal size (mm^3)	$0.3 \times 0.2 \times 0.1$
θ range for data collection (deg)	1.77–32.08
Index ranges	$-11 \le h \le 11$
	$-17 \le k \le 16$
	$-18 \le l \le 18$
Reflections collected	30206
Independent reflections	6819 [$R_{(int)} = 0.0355$]
Completeness to θ (max) (%)	96.1
Data/restraints/parameters	6819/0/199
GOF on F^2	0.808
Final R indices [$I > 2\sigma(I_0)$]	R1 = 0.0403
	wR2 = 0.1326
R indices (all data)	R1 = 0.0663
	wR2 = 0.2024
Largest diffraction peak/hole (e Å^{-3})	2.147 and −3.589

TABLE 2 Selected Bond Lengths (Å) and Bond Angles (°) for $(CH_3)_3Sn$ $(C_2H_2N_3S_2)$

Molecule A		Molecule B	
Bond lengths (Å)			
Sn1–C2	2.133 (5)	Sn2–C22	2.116 (6)
Sn1–C3	2.130 (5)	Sn2–C23	2.130 (5)
Sn1–C1	2.130 (5)	Sn2–C21	2.129 (5)
Sn1–S1	2.492 (13)	Sn2–S21	2.506 (14)
S1–C4	1.757 (5)	S21–C24	1.751 (5)
S2–C4	1.737 (5)	S22–C24	1.733 (5)
S2–C5	1.747 (5)	S22–C25	1.755 (5)
N1–C4	1.302 (6)	N21–C24	1.296 (6)
N2–C5	1.309 (6)	N22–C25	1.300 (6)
N3–C5	1.354 (6)	N23–C25	1.346 (6)
N1–N2	1.374 (5)	N21–N22	1.387 (6)
Bond angles (°)			
C4–S1–Sn1	98.41 (17)	C24–S21–Sn2	101.73 (16)
C1–Sn1–S1	103.61 (16)	C21–Sn2–S21	103.35 (16)
C2–Sn1–S1	104.04 (15)	C22–Sn2–S21	96.56 (17)
C3–Sn1–S1	102.75 (17)	C23–Sn2–S21	104.90 (16)
C2–Sn1–C1	111.6 (2)	C22–Sn2–C21	119.4 (3)
C2–Sn1–C3	116.5 (2)	C22–Sn2–C23	117.1 (2)
C3–Sn1–C1	116.2 (2)	C23–Sn2–C21	111.9 (2)
C4–S2–C5	87.3 (2)	C24–S22–C25	86.9 (2)
N1–C4–S2	113.1 (3)	N21–C24–S22	114.0 (3)
N1–C4 –S1	124.7 (3)	N21–C24–S21	123.9 (4)
C4–N1–N2	113.8 (4)	C24–N21–N22	113.0 (4)
C5–N2–N1	112.7 (4)	C25–N22–N21	112.9 (4)
N2–C5–S2	113.1 (3)	N22–C25–S22	113.1 (3)
N3–C5–S2	123.7 (4)	N23–C25–S22	122.8 (4)
S2–C4–S1	122.1 (3)	S22–C24–S21	122.0 (3)
N2–C5–N3	123.2 (4)	N22–C25–N23	124.0 (4)

with its symmetry-related molecules are also identified, viz., S1 − S22 = 3.573 Å [(x, y, z), (x, y, z)]; S2 − S21 = 3.570 Å [(x,y,z), (x,y, −1 + z)], N1 − N23 = 2.935 Å [(x, y, z), (x, y, z)], and N3 − N21 = 3.035 Å [(x,y,z), (x,y, −1 + z)]. These S − S contacts are less than the sum of the van der Waals radii of sulfur atoms (3.70 Å),[15] which may tend to hold the chains together. These interactions play an important role in the stabilization of the polymer by holding the monomers **a** and **b** together in an asymmetric unit (Figs. 3 and 4). In addition to this, intermolecular hydrogen bonding of type N–H···N also exists (Table 3), which is responsible for 1D chain structure of this complex. But, no intra-/intermolecular interactions between other ring nitrogen (i.e., N(2) and N(22)) and tin have been found.

CONCLUSIONS

(5-Amino-1,3,4-thiadiazolyl-2-thionato)trimethyltin(IV) crystallizes with a distorted tetrahedral geometry around tin. Two crystallographically distinct molecules **a** and **b** within the asymmetric unit are hydrogen bonded, and infinite 1D chains consisting of alternating, centrosymmetric R2,2(8) and

TABLE 3 Hydrogen-Bonding Geometry (Å, °)

D−H···A	D–H	H···A	D···A	D–H···A
N23–H23B...N1^{i}	0.86	2.11	2.935 (6)	159.71 (2)
N3–H3A...N22^{ii}	0.86	2.11	2.944 (7)	165.09 (2)
N23–H23A...N2^{ii}	0.86	2.28	3.075 (6)	154.14 (2)
N3–H3B...N21^{iii}	0.86	2.24	3.035 (6)	153.28 (2)

Symmetry codes: (i) x, y, z; (ii) −x, −y + 1, −z + 1; (iii) x, y, z − 1; (iv) x + 1, y, z + 1

R4,2(10) rings are generated by intermolecular "N–H–N" hydrogen bond interactions.

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Supplementary Material

CCDC No. 665110 contains the supplementary crystallography data of $Me_3Sn(C_2H_2N_3S_2)$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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