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Synthetic and Spectroscopic Investigations of Anions Containing the 1,3,2,4,5-Dithiadiazastannole Ring: X-ray Crystal Structure of [Ph_4As][$SnMe_2ClS_2N_2$]

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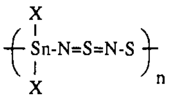
Received March 2, 1989

The reaction of the polymer $(SnCl_2S_2N_2)_n$ or the dimer $(SnMe_2S_2N_2)_2$ with chloride ions produces salts of the $SnCl_4S_2N_2^{2-}$ or $SnMe_2ClS_2N_2^-$ anions, respectively. X-ray structural determinations show that these anions contain the five-membered SnS_2N_2 ring. The crystals of [Ph_4As][$SnMe_2ClS_2N_2$] are triclinic with space group $P\bar{1}$, a = 11.036 (2) Å, b = 11.421 (2) Å, c 12.227 (3) Å, α = 77.75 (1)°, β = 80.28 (2)°, γ = 65.31 (1)°, V = 1362.6 (5) Å^3, and Z = 2. The final R and R_w values were 0.047 and 0.035, respectively. The $SnMe_2ClS_2N_2^-$ ion adopts a distorted trigonal-bipyramidal structure with equatorial methyl groups and a long axial Sn-Cl bond (2.652 (1) Å). The accuracy of the structural determination of the $SnCl_4S_2N_2^{2-}$ ion is low due to a crystal disorder caused by occupation of ca. 50% of the anion sites by the $SnCl_6^{2-}$ ion. A ^{119}Sn NMR investigation shows that the $SnCl_4S_2N_2^{2-}$ ion disproportionates to give $SnCl_6^{2-}$ in solution and, more slowly, in the solid state.

Introduction

Zuckerman et al. have reported that the reaction of anhydrous SnX_2 (X = Cl, Br) with S_4N_4 in CCl_4 produces insoluble, infusible solids of composition $SnX_2S_2N_2$.[1] The ^{119}Sn Mössbauer isomer shifts established the presence of Sn(IV) in these compounds, thus ruling out the possibility that they are tin(II) dihalide adducts of the four-membered S_2N_2 ring. Alternative structures involving either polymeric linear arrangements, **1**, or a cyclic form, **2**, of



$$\left(\overset{\overset{X}{|}}{\underset{\underset{X}{|}}{Sn}}\text{-}N{=}S{=}N\text{-}S \right)_n$$

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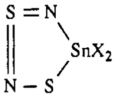

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the $SnX_2S_2N_2$ monomer units were considered but could not be distinguished on the basis of IR and ^{119}Sn Mössbauer spectroscopic data.[1] Although there is no precedent in the literature for polymers of type **1**, the ring system **2** (X = Me) has been structurally characterized and shown to form a dimer via two intermolecular Sn–N interactions.[2,3]

The reaction between $SnCl_2$ and S_4N_4 is of particular interest because it provides the standard route to $S_4N_4H_4$.[4] Hence, there is a possibility that the elucidation of the structures of the $SnX_2S_2N_2$ polymers will provide an explanation of the uniqueness of $SnCl_2$ as a reagent for this four-electron reduction process. The insoluble, infusible nature of $(SnX_2S_2N_2)_n$ may be the result of associated forms of **1** or **2** involving halogen bridges.[1] We have, therefore, prepared soluble derivatives by treatment of the polymer (X = Cl) with chloride ion and determined the X-ray structure of $[Ph_4As]_2[SnCl_4S_2N_2]$ so formed. This structural analysis revealed the presence of the five-membered SnS_2N_2 ring, but the accuracy of the data is low due to crystal disorder. Consequently, the salt [Ph_4As][$SnMe_2ClS_2N_2$] was prepared in order to provide a better structural and spectroscopic characterization of the SnS_2N_2 moiety. The possible involvement of $(SnCl_2S_2N_2)_n$ in the conversion of S_4N_4 into $S_4N_4H_4$ using $SnCl_2$ has also been investigated.

Experimental Section

General Procedure and Materials. CCl_4, CH_2Cl_2, and 1,2-$C_2H_4Cl_2$ were all dried by distillation from P_2O_5. CH_3CN was dried by distillation from CaH_2 and then from P_2O_5. S_4N_4[5] and $(Me_2SnS_2N_2)_2$[2] were prepared by the literature procedures. $SnCl_4$ (Aldrich) was distilled before use, and $SnCl_2$ (98%, Aldrich) was used as received. PPN^+Cl^- [PPN^+ = $(Ph_3P)_2N^+$] was prepared by the literature method[6] and was dried by heating to 60 °C under vacuum overnight. $Ph_4As^+Cl^-$ was obtained by heating $Ph_4As^+Cl^-{\cdot}xH_2O$ (Aldrich) at 111 °C under vacuum for 2 days. All distillations of solvents and all reactions were carried out under an atmosphere of dry nitrogen (99.99% purity). Chemical analyses were performed by the Analytical Services of the Department of Chemistry, University of Calgary.

Table I. ^{119}Sn NMR Chemical Shifts (ppm)

compd	solvent	δ[a]
$[PPN]_2[SnCl_4S_2N_2]$	CH_3CN	−26[b]
$[Ph_4As]_2[SnCl_4S_2N_2]$	CH_2Cl_2	−27.3
$Cs_2[SnCl_4S_2N_2]$[c]	CH_3CN	−29.5
[PPN][$SnMe_2ClS_2N_2$]	CH_3CN	+26
[Ph_4As][$SnMe_2ClS_2N_2$]	CH_3CN	+26
$[SnMe_2S_2N_2]_2$	1,2-$C_2H_4Cl_2$	+49
$[Ph_4As]_2[SnCl_6]$	1,2-$C_2H_4Cl_2$	−730[d]

[a] Chemical shifts (±2 ppm) are relative to Me_4Sn. A solution of Ph_3SnCl in $CDCl_3$ (δ −46.6) or $SnBr_4$ (50% in C_6D_6) (δ −633.1) was used as external reference for spectra that exhibited signals in the +325 to −25 ppm or −250 to −980 ppm regions, respectively. [b] A very weak peak at −732 ppm was also observed. [c] Prepared from CsCl and $(SnCl_2S_2N_2)_n$ (2:1) in acetonitrile. [d] The literature value for $[Bu_4N]_2[SnCl_6]$ in CH_2Cl_2 is −732 ppm.[7,8]

Instrumentation. Infrared spectra were recorded as Nujol mulls with CsI windows, on a Nicolet 5DX FT-IR spectrophotometer (400–4000 cm^{-1}). Raman spectra were recorded on a Jarrel-Ash Model 25-100 double monochromator, which was interfaced to an IBM-PC microcomputer to provide data acquisition and multiple-scan capabilities. A Coherent Radiation CR-4 argon ion laser was used to produce an exciting line at 514.4 nm (200 mW). Samples were run as pressed pellets of the pure compounds placed in glass vials and spun at ca. 1000 rpm to reduce laser-induced decomposition. At least eight scans were collected for each spectrum. Band positions were calibrated against CCl_4 and are reported with an accuracy of ±2 cm^{-1}.

^1H and ^{13}C NMR spectra were run on a Bruker ACE-200 spectrometer using a switchable 5-mm $^1H/^{13}C$ probe and the standard ^1H and ^{13}C parameters. The compounds were dissolved in $CDCl_3$ and referenced to external TMS. ^{119}Sn NMR spectra were obtained on a Varian XL-200 spectrometer operating at 74.55 MHz. The spectra were run unlocked by using a pulse width of 10 μs, an acquisition time of 0.25 s, and a line-broadening value of 40. ^{119}Sn NMR spectra were also recorded on an AM-400 Bruker 400-MHz instrument with a pulse width of 2 μs, an acquisition time of 0.033 s, and a line-broadening value of 10. At least 100 000 transients were collected for each sample spectrum. Chemical shifts are reported in ppm downfield from Me_4Sn.

Preparation of $(SnCl_2S_2N_2)_n$. The compound $(SnCl_2S_2N_2)_n$ was prepared by the reaction of S_4N_4 with anhydrous $SnCl_2$ in CCl_4 at reflux according to the literature procedure.[1] However, it was found that washing the product with CCl_4 was not sufficient to remove all traces of S_4N_4, so purification was achieved by Soxhlet extraction of crude $(SnCl_2S_2N_2)_n$ with carbon tetrachloride for 16 h.

Preparation of $[Ph_4As]_2[SnCl_4S_2N_2]$. $Ph_4As^+Cl^-$ (1.33 g, 3.18 mmol) and $(SnCl_2S_2N_2)_n$ (0.51 g, 1.81 mmol) in CH_2Cl_2 (30 mL) were stirred at 23 °C for 4 h. The orange-red solution was filtered to remove the

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(1) Das, M. K.; Bibber, J. W.; Zuckerman, J. J. *Inorg. Chem.* **1982**, *21*, 2864.

(2) Roesky, H. W.; Wiezer, H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 674.

(3) Roesky, H. W. *Z. Naturforsch.* **1976**, *31B*, 680.

(4) Brauer, G. *Handbook of Preparative Inorganic Chemistry*, 2nd ed.; Academic Press: New York, 1963; Vol. 1, p 411. The usual procedure involves the reaction of S_4N_4 in benzene at 80 °C with methanolic $SnCl_2{\cdot}2H_2O$.

(5) Villeno-Blanco, M.; Jolly, W. L. *Inorg. Synth.* **1967**, *9*, 98.

(6) Ruff, J. K.; Schlientz, W. J. *Inorg. Synth.* **1974**, *15*, 84.

(7) Colton, R.; Dakternieks, D.; Harvey, C. *Inorg. Chim. Acta* **1982**, *61*, 1.

(8) Dillon, K. B.; Marshall, A. *J. Chem. Soc., Dalton Trans.* **1987**, 315.

0020-1669/89/1328-3018$01.50/0

Table II. NMR (^1H and ^{13}C), IR, and Raman Spectroscopic Data for $[SnMe_2ClS_2N_2]^-$ and $[SnMe_2S_2N_2]_2$

	$[PPN]$-$[SnMe_2ClS_2N_2]$	$[Ph_4As]$-$[SnMe_2ClS_2N_2]$	$[SnMe_2S_2N_2]_2$[a]
		^1H NMR	
δ(Me), ppm	0.85	0.75	0.93
$J_{^1H-^{119}Sn}$, Hz	72.5	72.3	68.5
$J_{^1H-^{117}Sn}$, Hz	69.2	69.1	64.5
		^{13}C NMR	
δ(Me), ppm		8.2	*b*
$J_{^{13}C-^{119}Sn}$, Hz		543	
$J_{^{13}C-^{117}Sn}$, Hz		521	
		IR (cm^{-1})	
$\nu_{as}(SnC_2)$	*c*	545 m	552 m
$\nu_s(SnC_2)$	*c*	515 w	514 m
		Raman (cm^{-1})	
$\nu_{as}(SnC_2)$	536 w	540 w	556 w
$\nu_s(SnC_2)$	514 s	513 m	519 m
$\nu(S_2N_2)$	878 vs	894 vs	913 vs

[a] Literature values: δ(Me) −0.95, $J_{^1H-^{119}Sn} = 69.3$ Hz, $J_{^1H-^{117}Sn} = 66.3$ Hz.[2,14] [b] Not reported. [c] Obscured by cation bonds.

excess of $(SnCl_2S_2N_2)_n$ and slow evaporation (1 week) of solvent from the filtrate produced yellow crystals, which were recrystallized from CH_2Cl_2. Anal. Calcd for $C_{48}H_{40}As_2Cl_4N_2S_2Sn$: C, 51.51; H, 3.61; N, 2.51. Found: C, 49.73; H, 3.59; N, 1.99. An X-ray structural determination and ^{119}Sn NMR spectra (Table I) showed that these crystals contained $[Ph_4As]_2[SnCl_6]$ in addition to $[Ph_4As]_2[SnCl_4S_2N_2]$.

Preparation of $[PPN]_2[SnCl_4S_2N_2]$. PPN^+Cl^- (1.02 g, 1.77 mmol) and $(SnCl_2S_2N_2)_n$ (0.25 g, 0.88 mmol) in CH_2Cl_2 (30 mL) were stirred for 3 h at 23 °C. A small amount of white solid was removed from the yellow solution by filtration, and then solvent was removed under vacuum to give $[PPN]_2[SnCl_2S_2N_2]$ (1.13 g, 0.80 mmol) as a yellow solid. An analytical sample was obtained by recrystallization from CH_2Cl_2. Anal. Calcd for $C_{72}H_{60}Cl_4N_2P_4S_2Sn$: C, 60.48; H, 4.25; N, 3.92. Found: C, 59.76; H, 4.22; N, 3.14. The ^{119}Sn NMR spectrum showed that the product contained a small amount of $[PPN]_2[SnCl_6]$.

Preparation of $[Ph_4As][SnMe_2ClS_2N_2]$. A mixture of $Ph_4As^+Cl^-$ (0.60 g, 1.4 mmol) and $(SnMe_2S_2N_2)_2$ (0.17 g, 0.71 mmol) in acetonitrile (5 mL) was stirred at 23 °C for 9 h. Yellow crystals of $[Ph_4As]$-$[SnMe_2ClS_2N_2]$ were deposited from the resulting solution after 1 month. The structure of this salt was determined by X-ray crystallography. $[PPN][SnMe_2ClS_2N_2]$ was prepared in a similar manner from PPN^+Cl^- and $(SnMe_2S_2N_2)_2$. Spectroscopic data for these salts are given in Tables I and II.

Preparation of $[Ph_4As]_2[SnCl_6]$. A solution of $Ph_4As^+Cl^-$ (1.19 g, 2.84 mmol) in CH_2Cl_2 (30 mL) was added dropwise to $SnCl_4$ (0.39 g, 1.48 mmol). The reaction mixture was stirred for 10 min to give a white precipitate, which was removed by filtration and recrystallized from CH_2Cl_2 to give $[Ph_4As]_2[SnCl_6]$ (1.26 g, 1.18 mmol). ^{119}Sn NMR spectroscopic data are given in Table I.

Attempted Preparation of $S_4N_4H_4$ from $(SnCl_2S_2N_2)_n$. A mixture of methanol (7 mL) and water (0.7 mL) was added slowly to a slurry of $(SnCl_2S_2N_2)_n$ (1.17 g, 4.15 mmol) in boiling 1,2-dichloroethane (11 mL). The reaction mixture was stirred at reflux for 6 h and then cooled to −30 °C. A small amount of sulfur was isolated, but there was no evidence for the formation of $S_4N_4H_4$.

X-ray Analysis. A suitable transparent block-shaped crystal was wedged in a glass capillary, and mounted on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters and their standard deviations were derived from the setting angles of 25 reflections in the range $9.5 < \theta < 15.2°$. Reduced cell calculations did not indicate any higher metric symmetry. Crystal and instrumental instability were monitored through the measurement of three standard reflections every 3 h of X-ray exposure time; there was no indication of crystal decomposition. The net intensities of the data were corrected for reflection width, scale variation, Lorentz, and polarization effects. Variance $\sigma^2(I)$ was calculated on the basis of counting statistics. Crystal data and experimental details of the structure determination are compiled in Table III.

The Sn and As atoms and the two sulfur atoms were located in an *E* map with phases derived from symbolic addition.[9a] The remaining non-hydrogen atoms were located in difference maps after refining the scale and thermal parameters. At this stage of the refinement all of the hydrogen atoms were located in difference Fourier maps. All non-hydrogen atoms were refined with anisotropic temperature factors, with the hydrogens refined with independent isotropic temperature factors. Convergence was reached at $R = 0.047$. The final values of the refined positional parameters, tables of hydrogen atom positions, thermal parameters, comprehensive lists of bond distances and angles, and tables of F_o, F_c, and $\sigma(F)$ are available as supplementary material. Neutral-atom scattering factors were used with anomalous dispersion corrections applied.[10] All calculations were carried out on a VAX 11/780 at the University of Calgary with the program package XTAL.[9b]

Table III. Crystallographic Parameters for $[Ph_4As][SnMe_2ClS_2N_2]$

formula $C_{26}H_{26}AsClN_2S_2Sn$	fw 659.70
$a = 11.036$ (2) Å	space group $P\bar{1}$
$b = 11.421$ (2) Å	$T = 25$ °C
$c = 12.227$ (3) Å	$\lambda = 0.71069$ Å (Mo Kα; graphite monochromator)
$\alpha = 77.75$ (1)°	$\rho_{calc} = 1.608$ g cm^{-3}
$\beta = 80.28$ (2)°	$\mu = 23.06$ cm^{-1}
$\gamma = 65.31$ (1)°	$R = 0.046$
$V = 1362.6$ (5) Å^3	$R_w = 0.035$
$Z = 2$	

Results and Discussion

Preparation of Salts of the $SnCl_4S_2N_2^{2-}$ and $SnMe_2ClS_2N_2^-$ Ions. The association of monomer units in **1** or **2** (X = Cl, Br) is likely due to halogen bridges,[1] so the extended structure should be disrupted by reaction with halide ions. This approach has been used to prepare transition-metal complexes of the type $Cl_xMS_2N_3^-$ ($x = 3$, M = V; $x = 4$, M = Mo, W) from the corresponding dimers (M = Mo, W)[11,12] or polymers (M = V).[13] Accordingly, the reaction of $(SnCl_2S_2N_2)_n$ with chloride ions in CH_2Cl_2 was investigated and produced soluble, yellow salts of the $SnCl_4S_2N_2^{2-}$ ion in good yield.

$$(SnCl_2S_2N_2)_n + 2MCl \rightarrow M_2[SnCl_4S_2N_2] \quad (M = Cs, Ph_4As, PNP) \tag{1}$$

An excess of chloride ion should be avoided in the preparation of the $SnCl_4S_2N_2^{2-}$ ion in order to prevent the formation of $SnCl_6^{2-}$. These salts also undergo disproportionation to give $SnCl_6^{2-}$ in the solid state or, more rapidly, in solution, as indicated by the structural and spectroscopic data described below.

The related anion $SnMe_2ClS_2N_2^-$ was also prepared in high yield by the reaction of **2** (X = Me) with chloride ion in acetonitrile.

$$(SnMe_2S_2N_2)_2 + 2MCl \rightarrow 2M[SnMe_2ClS_2N_2] \quad (M = Ph_4As, PNP) \tag{2}$$

NMR (^1H and ^{13}C), IR, and Raman spectroscopic data for the $SnMe_2ClS_2N_2^-$ ion are given in Table II. The ^1H and ^{13}C NMR spectra both show singlets consistent with equivalent methyl groups. The J_{Sn-^1H} coupling constants are ca. 4 Hz larger than the corresponding values for $[SnMe_2S_2N_2]_2$, indicating larger s-orbital contributions in the Sn–C bonds of the anion. The asymmetric and symmetric SnC_2 stretching vibrations are observed in both the IR and Raman spectra, suggesting a bent $SnMe_2$ group. Thus, the spectroscopic data for $[SnMe_2ClS_2N_2]^-$ indicate a trigonal-bipyramidal structure with equatorial methyl groups. The dominant feature of the Raman spectra of species containing the SnS_2N_2 group is a very strong band in the 880–910-cm^{-1} region.

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(9) (a) Schlenk, H.; Hall, S. R. "SIMPEL"; *XTAL 2.4 User's Manual*; Hall, S. R., Stewart, J. M., Eds.; Universities of Western Australia and Maryland, 1988. (b) Hall, S. R.; Stewart, J. M., Eds. *XTAL 2.4 User's Manual*; Universities of Western Australia and Maryland, 1988.

(10) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.

(11) Kynast, U.; Conradi, E.; Müller, U.; Dehnicke, K. *Z. Naturforsch.* **1984**, *39B*, 1680.

(12) Anhaus, J.; Siddiqi, Z. A.; Schimkowiak, J.; Roesky, H. W. *Z. Naturforsch.* **1984**, *39B*, 1722.

(13) Hanich, J.; Krestel, M.; Müller, U.; Dehnicke, K. *Z. Naturforsch.* **1984**, *39B*, 1686.

(14) The chemical shift of $(SnMe_2S_2N_2)_2$ is given incorrectly as δ −0.95 in ref 2.

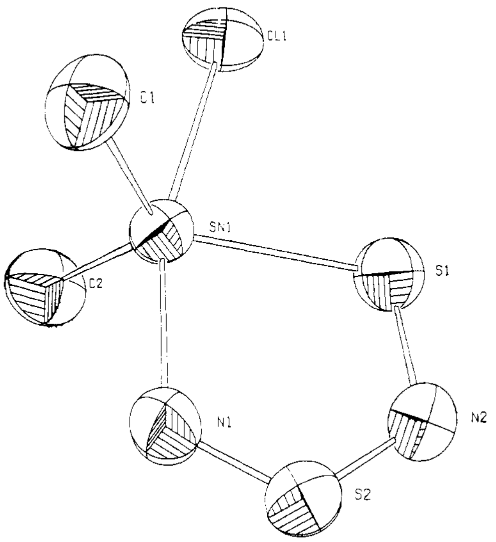

Figure 1. ORTEP plot (50% probability ellipsoids) showing the atomic numbering scheme for the anion in $[Ph_4As][SnMe_2ClS_2N_2]$.

X-ray Crystal Structures of $[Ph_4As]_2[SnCl_4S_2N_2]$ and $[Ph_4As][SnMe_2ClS_2N_2]$. An X-ray structural determination of $[Ph_4As]_2[SnCl_4S_2N_2]$ has identified the SnS_2N_2 unit as a 1,3,2,4,5-dithiadiazastannole ring. However, the accuracy of the structural analysis is low due to a crystal disorder caused by occupation of ca. 50% of the anion sites by the structurally similar $SnCl_6^{2-}$ ion.[15] In order to provide a better structural characterization of the SnS_2N_2 ring, the X-ray structure of $[Ph_4As][SnMe_2ClS_2N_2]$ was determined. An ORTEP plot of the anion is shown in Figure 1, and the structural parameters are compared with those of the dimer of **2** (X = Me) in Table IV. It should be noted that the N(2) and Sn atoms in the dimer are three- and five-coordinate, respectively, due to the occurrence of intermolecular Sn–N bonds.[16] The geometry about tin in the $SnMe_2ClS_2N_2^-$ ion is distorted trigonal bipyramidal with two methyl groups in equatorial positions, the chlorine atom in an axial position, and the chelating $S_2N_2^{2-}$ ligand occupying the axial and equatorial vacancies. The three bond angles in the trigonal plane are all close to 120°, but the axial substituents are in a distinctly nonlinear arrangement with Cl(1)–Sn–S(1) = 80.61 (4)° and N(1)–Sn–S(1) = 83.07 (9)°. The methyl groups are bent away from N(1) toward Cl(1) with average bond angles for C–Sn–N(1) and C–Sn–Cl(1) of 96.8 (3) and 91.2 (2)°, respectively. The Sn–Cl bond distance of 2.652 (1) Å is long even for an axial bond (cf. 2.42 Å in $SnMe_3Cl\cdot$pyridine[17] and an average value of 2.54 (2) Å for the two axial bonds in the $SnMe_2Cl_3^-$ anion[18]). However, bond lengths of 2.696 (3) and 2.572 (4) Å have been reported for the axial bonds in $Me_3SnCl_2^-$.[19] The pattern of S–N bond lengths within the SnS_2N_2 ring follows the sequence found for other MS_2N_2 rings,[20] i.e. long [1.691 (4) Å], short [1.568 (4) Å], short [1.496 (3) Å], indicating a tendency toward localization of π-bonding with the thiazene unit. The actual values closely resemble those found for $(H_3N)PbS_2N_2$ [1.717 (7), 1.557 (4) and 1.508 (7) Å].[21]

Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) for $SnMe_2ClS_2N_2^-$ and $(Me_2SnS_2N_2)_2$

	$SnMe_2ClS_2N_2^-$	$(SnMe_2S_2N_2)_2$[a]
Sn–S(1)	2.469 (1)	2.603
S(1)–N(2)	1.691 (4)	1.673
N(2)–S(2)	1.568 (4)	1.602
S(2)–N(1)	1.496 (3)	1.552
N(1)–Sn	2.176 (4)	2.135
Sn–C(2)	2.118 (5)	2.123
Sn–C(1)	2.123 (7)	2.084
Sn–Cl(1)	2.652 (1)	
Sn–S(1)–N(1)	102.8 (1)	103.2
S(1)–N(2)–S(2)	118.4 (2)	118.1
N(2)–S(2)–N(1)	118.4 (2)	116.8
S(2)–N(1)–Sn	117.3 (2)	121.0
S(1)–Sn–N(1)	83.07 (9)	80.8
S(1)–Sn–Cl	80.61 (4)	
C(1)–Sn–Cl	91.1 (2)	
C(2)–Sn–Cl	91.4 (2)	
C(1)–Sn–N(1)	96.5 (3)	
C(2)–Sn–N(1)	97.1 (2)	
C(1)–Sn–C(2)	120.4 (2)	
C(1)–Sn–S(1)	120.6 (2)	
C(2)–Sn–S(1)	118.5 (2)	

[a] Data taken from ref 16 (esd's not given).

^{119}Sn NMR Spectra. A ^{119}Sn NMR spectroscopic investigation of the anions prepared in this study was carried out in order to determine the characteristic chemical shifts of the SnS_2N_2 ring system and to monitor the formation of $SnCl_6^{2-}$ from $SnCl_4S_2N_2^{2-}$. The ^{119}Sn NMR data are summarized in Table I. The ^{119}Sn chemical shift of $SnCl_4S_2N_2^{2-}$ occurs at –28 ± 2 ppm in all three salts. For comparison, the $SnMe_2ClS_2N_2^{2-}$ ion shows a singlet at +26 ppm, indicating that the replacement of two chlorines by two methyl groups in this anion causes a relatively small change in the electronic environment in tin. By contrast, the ^{119}Sn chemical shift of the $SnCl_6^{2-}$ ion is observed at ca. –730 ppm[7,8] so that the chelating $S_2N_2^{2-}$ ion imposes a remarkable deshielding effect on the ^{119}Sn NMR chemical shift.

The $SnCl_4S_2N_2^{2-}$ ion disproportionates in solution, particularly in chlorocarbon solvents, to give $SnCl_6^-$. For example, the ^{119}Sn NMR spectrum of a solution of $[Ph_4As]_2[SnCl_4S_2N_2]$ in 1,2-$C_2H_4Cl_2$ after standing for 5 months exhibits only one signal at –730 ppm. This transformation also occurs slowly in the solid state. A freshly prepared sample of $[PPN]_2[SnCl_4S_2N_2]$ shows a very weak peak at –732 ppm, whereas a year-old sample of the same compound displays only this peak, and the signal for $SnCl_4S_2N_2^{2-}$ is no longer observed. This disproportionation reaction probably accounts for the presence of $SnCl_6^{2-}$ in the crystal used for the X-ray structural investigation of $SnCl_4S_2N_2^{2-}$, but the fate of the S_2N_2 ligand in this transformation is unknown.

Attempted Synthesis of $S_4N_4H_4$ from $(SnCl_2S_2N_2)_n$. The possibility that the 1,3,2,4,5-dithiadiazastannole ring might be involved as an intermediate in the standard synthesis of $S_4N_4H_4$[4] was investigated by subjecting a slurry of $(SnCl_2S_2N_2)_n$ and aqueous methanol to reflux in 1,2-dichloroethane. The only sulfur-containing product isolated, however, was a small amount of *c*-S_8. It appears, therefore, that the SnS_2N_2 moiety is not involved as an intermediate in the synthesis of $S_4N_4H_4$.

Summary. The anions $SnCl_4S_2N_2^{2-}$ and $SnMe_2ClS_2N_2^-$, prepared by the addition of Cl^- ions to $(SnCl_2S_2N_2)_2$ and $(SnMe_2S_2N_2)_2$, respectively, contain the 1,3,2,4,5-dithiazastannole ring. This finding indicates that the polymers obtained from the reactions of tin(II) halides with S_4N_4 also involve the SnS_2N_2 ring.

Acknowledgment. We thank the NSERC (Canada) for financial support in the form of operating grants, a postgraduate fellowship (K.J.S.), and an infrastructure grant for the X-ray structure service and Dr. K. A. Kerr for use of the X-ray diffractometer. The assistance of Dr. R. Kydd (Raman spectra) is also gratefully acknowledged.

Supplementary Material Available: Tables SI–SVII, listing crystallographic parameters, positional and isotropic thermal parameters for non-H and H atoms, anisotropic thermal parameters for non-H atoms, and bond lengths, bond angles, and torsion angles for non-H atoms (7 pages); tables of observed and calculated structure factors (57 pages). Ordering information is given on any current masthead page.

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(15) Richardson, J. F. Private communication.
(16) Roesky, H. W. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 254.
(17) Hulme, R. *J. Chem. Soc.* **1963**, 1524.
(18) Einstein, F. W. B.; Penfold, B. R. *J. Chem. Soc. A* **1968**, 3019.
(19) Vergamini, P. J.; Vahrenkamp, H.; Dahl, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 6327.
(20) Chivers, T.; Edelmann, F. *Polyhedron* **1986**, *5*, 1661.
(21) Martan, H.; Weiss, J. *Z. Anorg. Allg. Chem.* **1984**, *514*, 107.