Table X. Average Sn–O and Sn–S Bond Lengths (Å) for the Cyclic Stannates **1–4**

compd	coord no.	Sn–S[a]	Sn–O[a]	Sn–O[b]
1	5	2.457 (2)		
2	5	2.397 (2)	2.054 (5)	
3	6	2.436 (3)		2.164 (7)
4	6		2.051 (5)	2.086 (4)

[a] Non-hydrogen bonded. [b] Hydrogen bonded.

to 96.1 (2)°. Evidence of the hydrogen-bonding interaction is found in the Sn–O2 bond length of 2.086 (4) Å, which is somewhat lengthened compared to the Sn–O1 and Sn–O3 bonds, with lengths of 2.049 (5) and 2.052 (4) Å, respectively.

A comparison of average values of Sn–S and hydrogen-bonded and non-hydrogen-bonded Sn–O bond lengths (Table X) shows that hydrogen bonding produces the most pronounced lengthening effect in **3**. The latter has O–H–O hydrogen bonding compared to the apparently weaker interaction N–H–O in **4**. No bond length effect is discernible accompanying the change in coordination number encountered between **1–2** and **3–4**.

Structural Comparisons. The spirocyclic stannates **1** and **2** give the expected structures. The general rule for five-coordinated anionic tin,[14] as with related germanium[9,27,28] and silicon[29-32] derivatives and the isoelectronic phosphoranes,[33,34] arsoranes,[35,36] and stiboranes,[37,38] is that wherever two unsaturated five-membered rings are present containing like atoms in each ring system bonded to the central atom, the resulting structure is rectangular pyramidal. Introduction of dissimilar bonding ring atoms, as in **2**, allows the apicophilicity rule[39,40] to take preference over the ring-strain effect[41] and causes structural displacement back to the inherently more stable trigonal bipyramid. The operation of these effects are apparent in examination of the data in Table I.

Conclusion. Ring-containing pentacoordinated anionic tin complexes prefer Sn–S to Sn–O bonding. The tendency to form M–O bonding in such systems increases from tin to germanium to silicon. For pentacoordinated anionic silicon(IV), no examples of ring Si–S bonding are known.[29-32] The special stability of ring Sn–S bonding in these compounds is attributed to a proper balance of the effects of low tin atom electronegativity vs the tendency of tin to increase its coordination number. Increased tin acidity provided by Sn–O bonds appears to favor the formation of hexacoordinated species.

Acknowledgment. The support of this research by the National Science Foundation (Grant CHE8504737) is gratefully acknowledged. We also thank the University of Massachusetts Computing Center for generous allocation of computer time.

Supplementary Material Available: Thermal parameters, hydrogen atom parameters, and additional bond lengths and angles (Tables S1–S3, respectively, for **1**, Tables S4–S6 for **2**, Tables S7–S9 for **3**, and Tables S10–S12 for **4**) (18 pages); listings of observed and calculated structure factor amplitudes for **1–4** (37 pages). Ordering information is given on any current masthead page.

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[27] Holmes, R. R.; Day, R. O.; Sau, A. C.; Holmes, J. M. *Inorg. Chem.* **1986**, *25*, 600–606.

[28] Holmes, R. R.; Day, R. O.; Sau, A. C.; Poutasse, C. A.; Holmes, J. M. *Inorg. Chem.* **1986**, *25*, 607–611.

[29] Holmes, R. R.; Day, R. O.; Chandrasekhar, V.; Harland, J. J.; Holmes, J. M. *Inorg. Chem.* **1985**, *24*, 2016–2020.

[30] Holmes, R. R.; Day, R. O.; Chandrasekhar, V.; Holmes, J. M. *Inorg. Chem.* **1985**, *24*, 2009–2015.

[31] Holmes, R. R.; Day, R. O.; Harland, J. J.; Holmes, J. M. *Organometallics* **1984**, *3*, 347–353.

[32] Holmes, R. R.; Day, R. O.; Harland, J. J.; Sau, A. C.; Holmes, J. M. *Organometallics* **1984**, *3*, 341–347.

[33] Reference 13, Chapter 2.

[34] Holmes, R. R. *Prog. Inorg. Chem.* **1984**, *32*, 119–235, and references cited therein.

[35] Holmes, R. R.; Day, R. O.; Sau, A. C. *Organometallics* **1985**, *4*, 714–720.

[36] Poutasse, C. A.; Day, R. O.; Holmes, J. M.; Holmes, R. R. *Organometallics* **1985**, *4*, 708–713.

[37] Holmes, R. R.; Day, R. O.; Chandrasekhar, V.; Holmes, J. M. *Inorg. Chem.* **1987**, *26*, 157.

[38] Holmes, R. R.; Day, R. O.; Chandrasekhar, V.; Holmes, J. M. *Inorg. Chem.* **1987**, *26*, 163–168.

[39] Holmes, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 433–446.

[40] Holmes, R. R. *Pentacoordinated Phosphorus*; ACS Monograph 176; American Chemical Society: Washington, DC, 1980; p 32f.

[41] Holmes, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 5379–5385.

Hydrolysis Reactions Leading to Ring-Containing Hexacoordinated Distannoxanes. Tin–Sulfur vs Tin–Oxygen Bonding[1,2]

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Abstract: Hydrolysis reactions employing $SnCl_4{\cdot}5H_2O$ with either disodium mercaptoethanolate or disodium dimercaptomaleonitrile in the presence of Et_4NCl yield the new distannates $[(C_2H_4OS)_2SnCl]_2[H][Et_4N]$ (**2**) and $[((CN)_2C_2S_2)_2SnOH]_2[Et_4N]_2$ (**3**), respectively, possessing the four-membered Sn_2O_2 ring unit in cyclized hexacoordinated tin products. Their formation most likely proceeds via five-coordinated spirocyclic intermediates in which the integrity of the tin–sulfur bonding system is maintained as the distannoxane rings form. In agreement with previous results, the formation of tin–oxygen bonding is conducive in stabilizing tin(IV) in the dianionic hexacoordinated state while tin–sulfur bonding is preferred over tin–oxygen bonding in pentacoordinated anionic tin species. Hydrolysis of *n*-butyltin trichloride leads to the distannate $[n\text{-}BuSn(OH)(OH_2)Cl_2]_2$ (**1**), whose structure again contains hexacoordinated tin atoms in a Sn_2O_2 ring arrangement. **1** crystallizes in the monoclinic space group $P2_1/n$ with $a = 6.047$ (1) Å, $b = 25.090$ (6) Å, $c = 6.556$ (1) Å, $\beta = 107.16$ (1)°, and $Z = 2$. **2** crystallizes in the monoclinic space gruop $P2_1/n$ with $a = 12.522$ (2) Å, $b = 8.808$ (1) Å, $c = 26.000$ (2) Å, $\beta = 104.32$ (1)°, and $Z = 4$. **3** crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.841$ (2) Å, $b = 11.201$ (2) Å, $c = 11.932$ (2) Å, $\alpha = 65.39$ (1)°, $\beta = 76.01$ (1)°, $\gamma = 80.17$ (1)°, and $Z = 1$. The final conventional unweighted agreement factors were 0.037 (**1**), 0.034 (**2**), and 0.032 (**3**).

The ready formation of the four-membered cyclic distannoxane unit, Sn_2O_2, in hydrolysis reactions of mono- and diorganotin compounds is well-known. As early as 1858 Strecker[4] formed $IEt_2SnOSnEt_2I$ by heating diethyltin oxide with diethyltin diiodide.

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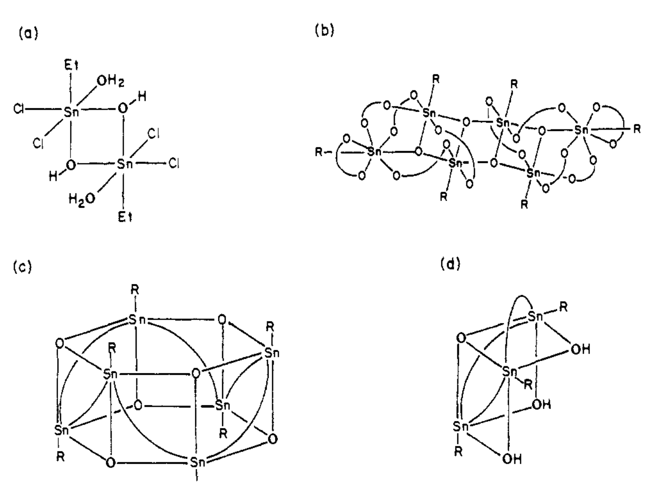
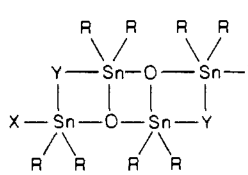


Figure 1. Schematic representations of organotin structures containing the four-membered distannoxane ring unit, $(Sn-O)_2$: (a) $[EtSn(OH)(OH_2)Cl_2]_2$;[16] (b) open-drum or ladder,[18-19] $[(RSn(O)O_2R')_2RSn(O_2R')_3]_2$; (c) drum,[17-19] $[RSn(O)O_2R']_6$; (d) oxygen-capped cluster,[22] $[(n\text{-}BuSn(OH)O_2PPh_2)_3O][Ph_2PO_2]$. In (d), only the cation is shown. The bidentate acid functions $R'O_2$ are represented by curved lines connecting adjacent tin atoms.

Since then, formulations of this type have been found to belong to a class of tetraorganodistannoxanes represented as dimeric[5-8] $[XR_2SnOSnR_2X]_2$ and possessing the general structural arrangement where R = alkyl or aryl and X and Y may be the same



or different, e.g., halogen, hydroxide, or isothiocyanate.[9-13] Besides the method used by Strecker, these distannoxanes may be prepared by the base hydrolysis of diorganotin dihalides.[7] We reported[13] the first X-ray structure of the aryl derivatives $[Ph_2(Cl)SnOSnPh_2(OH)]_2\cdot 2Me_2CO$ and $[Ph_2(Cl)SnOSnPh_2(Cl)]_2$ prepared this way. Puff et al.[10] reported the X-ray structure of a rare example of the fully hydroxylated distannoxane $[(Me_3SiCH_2)_2(OH)Sn-O-Sn(Me_3SiCH_2)_2(OH)]_2$. All of these structures have a planar ladder arrangement with distorted trigonal-bipyramidal geometries about the five-coordinated tin centers.

However, the cyclic distannoxane unit is not confined to these compounds alone. It is also present in hydrolysis products of monoorganotin compounds,[14,15] e.g., in the derivative $[EtSn(OH)(OH_2)Cl_2]_2$[16] and in new structural classes of organotin oxy carboxylate compositions, $[RSn(O)O_2CR']_6$[17-19] and $[(RSn(O)O_2CR')_2RSn(O_2CR')_3]_2$.[18,19] The latter substances may be prepared from a condensation reaction between a stannoic acid and a carboxylic acid[20] or, in the case of the dimeric composition, by reacting an organotin trichloride with the silver salt of the corresponding acid,[21] followed by hydrolysis. They have "drum"[17-19] and "open drum"[18,19] or "ladder" structures, respectively, as determined by X-ray analysis. We recently reported a related example, an oxygen-capped cluster, $[(n\text{-}BuSn(OH)O_2PPh_2)_3O][Ph_2PO_2]$,[22] having a partial cubelike structure. All of these compositions have hexacoordinated tin atoms, except the dimeric mixed oxy carboxylate–tricarboxylates,[18,19] which occasionally have end-capped seven-coordinated tin atoms in addition to the presence of six-coordinated tin atoms. Schematic representations based on X-ray determinations are shown in Figure 1. It is interesting that, in common with other stannoxane compositions, either one, three, or six distannoxane rings are present in the structural representations.

In related papers,[1b,23,24] we have demonstrated the strong preference for tin–sulfur bonding in five-coordinated anionic tin compounds compared to tin–oxygen bonding. Introduction of tin–oxygen bonding appears to be more conducive to the formation of dianionic hexacoordinated tin.[1b] In this sense, it would be interesting to examine the relative ease of formation of tin–sulfur and tin–oxygen bonding in hexacoordinated tin complexes. In the present work we attempt to do this by exploring the coexistence of these two types of tin bonding in new distannoxanes. The derivatives $[(C_2H_4OS)_2SnCl]_2[H][Et_4N]$ (**2**) and $[((CN)_2C_2S_2)_2SnOH]_2[Et_4N]_2$ (**3**) are formed in hydrolysis reactions from tin tetrachloride pentahydrate and the disodium salts of mercaptoethanol and dimercaptomaleonitrile, respectively. Also, the initial stages of hydrolysis of n-butyltin trichloride leading to $[n\text{-}BuSn(OH)(OH_2)Cl_2]_2$ (**1**) is examined, and the X-ray structural determinations of **1**–**3** are reported.

Experimental Section

All solvents were either used directly from freshly opened bottles or dried prior to use. Acetonitrile was refluxed and distilled from phosphorus pentoxide. Reagents, n-butyltin trichloride, tin tetrachloride pentahydrate, and o-mercaptoethanol, were from commercial sources (Aldrich Co.) and were used without further purification.

^1H NMR spectra were obtained on a Varian A-60 spectrometer. Additional ^1H NMR spectra and ^{119}Sn NMR spectra were recorded on a Varian XL-300 system operating in the pulsed Fourier transform mode at 300.0 and 111.862 MHz, respectively. Chemical shifts are reported with reference to tetramethylsilane (^1H) and tetramethyltin (^{119}Sn). Infrared spectra were recorded on a Perkin-Elmer Model 180 spectrometer. Nujol was used as the mulling agent.

Disodium dimercaptomaleonitrile was synthesized according to a published procedure.[25] Melting points were obtained with a Uni-melt capillary melting point apparatus (Hoover) and were uncorrected. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts.

Syntheses. Di-n-butyltetrachlorodiaquobis(μ-hydroxy)distannate, $[n\text{-}BuSn(OH)(OH_2)Cl_2]_2$ (1). n-Butyltin trichloride (1.0 g, 3.6 mmol) was

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(1) (a) Pentacoordinated Molecules. 71. (b) Part 70: Holmes, R. R.; Shafieezad, S.; Chandrasekhar, V.; Sau, A. C.; Holmes, J. M.; Day, R. O. *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) Presented in part at the 192nd National Meeting of the American Chemical Society, Anaheim, CA, Sept 1986; paper INOR 220.

(3) This work represents in part a portion of: Shafieezad, S. Ph.D. Thesis, University of Massachusetts, Amherst, MA, 1986.

(4) Strecker, A. *Annalen.* **1858**, *123*, 365–372.

(5) Okawara, R.; Wada, M. *J. Organomet. Chem.* **1963**, *1*, 81–88.

(6) Alleston, D. L.; Davies, A. G.; Hancock, M. *J. Chem. Soc.* **1964**, 5744–5748.

(7) Alleston, D. L.; Davies, A. G.; Hancock, M.; White, R. F. M. *J. Chem. Soc.* **1963**, 5469–5475.

(8) Okawara, R.; Wada, M. *Adv. Organomet. Chem.* **1967**, *5*, 137–167, and references cited therein.

(9) Harrison, P. G.; Begley, M. J.; Molloy, K. C. *J. Organomet. Chem.* **1980**, *186*, 213–236.

(10) Puff, H.; Friedrichs, E.; Visel, F. *Z. Anorg. Allg. Chem* **1981**, *477*, 50–58.

(11) Chow, Y. M. *Inorg. Chem.* **1971**, *10*, 673–677.

(12) Puff, H.; Bung, I.; Friedrichs, E.; Jansen, A. *J. Organomet. Chem.* **1983**, *254*, 23–32.

(13) Vollano, J. F.; Day, R. O.; Holmes, R. R. *Organometallics* **1984**, *3*, 745–750.

(14) Luijten, J. G. A. *Recl. Trav. Chim. Pays-Bas* **1966**, *85*, 873–878.

(15) Blunden, S. J.; Smith, P. J.; Gillies, D. G. *Inorg. Chim. Acta* **1982**, *60*, 105–109.

(16) Lecomte, C.; Protas, C. L.J.; Devaud, M. *Acta Crystallogr., Sect.B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 923–924.

(17) Chandrasekhar, V.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1985**, *24*, 1970–1971.

(18) Holmes, R. R.; Schmid, C. G.; Chandrasekhar, V.; Day, R. O.; Holmes, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 1408–1414.

(19) Chandrasekhar, V.; Schmid, C. G.; Burton, S. D.; Holmes, J. M.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1987**, *26*, 1050–1056.

(20) (a) Lambourne, H. *J. Chem. Soc.* **1922**, *121*, 2533–2540. (b) *Ibid.* **1924**, *125*, 2013–2015.

(21) Anderson, H. H. *Inorg. Chem.* **1964**, *3*, 912–914.

(22) Day, R. O.; Holmes, J. M.; Chandrasekhar, V.; Holmes, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 940–941.

(23) Day, R. O.; Holmes, J. M.; Shafieezad, S.; Chandrasekhar, V.; Holmes, R. R., submitted for publication.

(24) Holmes, R. R.; Shafieezad, S.; Holmes, J. M.; Day, R. O. *Inorg. Chem.* **1988**, *27*, in press.

(25) Davison, A.; Holm, R. H. *Inorg. Synth.* **1967**, *10*, 18–26.

taken in a vial and left exposed to air, allowing atmospheric moisture to slowly hydrolyze the chloride. After 1 week flaky crystals were isolated: yield 100 mg (10%); mp 125–132 °C (lit.[15] mp 73–120 °C); ^{1}H NMR ($CDCl_3$) ($SnC\bar{H}_2C\bar{H}_2C\bar{H}_2C\bar{H}_3$) 2.40 [t, $CH_2(a)$], 1.94 [m, $CH_2(b)$], 1.56 [m, $CH_2(c)$], 1.22 [t, $CH_3(d)$], [(a) refers to the α-CH_2 protons, etc.], 1.6 ($SnOH$, $SnOH_2$, br), $^2J(^{119}Sn–C–^1H)$ = 90.0 Hz; ^{119}Sn NMR (acetone-d_6) −208.7 (low intensity), −408.6 (major peak) (The ratio of the two signal intensities is roughly 1:10); IR (Nujol) 3360 (br, ν_{OH}), 655 ($\nu_{Sn–O}$). Anal. Calcd for $C_4H_{12}O_2Cl_2Sn$: C, 17.05; H, 4.30. Found: C, 16.60; H, 3.88.

Hydrogen Tetraethylammonium Dichlorobis(mercaptoethanolato)bis(μ-mercaptoethanolato-O,O')distannate $[(SCH_2CH_2O)_2SnCl]_2[H][Et_4N]$ (2). Tin tetrachloride pentahydrate (1.9 g, 5.4 mmol) was dissolved in acetonitrile (30 mL) and stirred. Disodium mercaptoethanolate, which was prepared by mixing sodium (0.5 g, 21.7 mmol) and mercaptoethanol (0.761 mL, 12.1 mmol) in methanol, was placed in a dropping funnel. Dropwise addition caused the immediate formation of a white solid. After the addition was completed, tetraethylammonium chloride (0.89 g, 5.4 mmol) was added, and the mixture was heated at 50 °C for 1 h. After filtering, the solvent was removed by evaporation under vacuum to yield a viscous colorless oil. The colorless oil was dissolved in 5 mL of acetonitrile, and the resultant mixture was treated with 10 mL of diethyl ether and cooled for several weeks to yield colorless crystals: mp 127–130 °C; ^{1}H NMR (CD_3CN) 1.15 (t, 12 H), 3.1 (q, 8 H), 2.7–3.0 (m, 4 H), 3.3–4.0 (m, 4 H). Anal. Calcd for $C_{16}H_{37}Cl_2O_4S_4NSn_2$: C, 25.83; H, 5.01. Found: C, 26.35; H, 5.19. Crystals suitable for X-ray analysis were grown from a mixture of acetonitrile and ether at 0 °C.

Bis(tetraethylammonium) Tetrakis(dicyanoethylene-1,2-dithiolato)bis(μ-hydroxy)distannate (IV), $[((CN)_2C_2S_2)_2SnOH]_2[Et_4N]_2$ (3). Tin tetrachloride pentahydrate (1.0 g, 2.8 mmol) was dissolved in ethanol (20 mL) and stirred. Disodium *cis*-1,2-dicyano-1,2-ethylenedithiolate (1.02 g, 5.5 mmol) was added to the above solution, and the resulting solution was stirred at room temperature for 0.5 h. Tetraethylammonium chloride (0.458 g, 2.8 mmol) was added to the solution mixture, and it was stirred for an additional 1 h. After filtering, the yellow solution was evaporated under vacuum to dryness. The yellow solid that formed was washed with water and air-dried. The resultant solid was dissolved in 10 mL of acetonitrile, treated with 10 mL of diethyl ether, and cooled to yield yellow crystals: yield 0.678 g (44%); mp 172–175 °C; ^{1}H NMR (CD_3CN) 1.17 (t, 12 H), 3.15 (q, 8 H). Anal. Calcd for $C_{32}H_{42}N_{10}O_2S_8Sn_2$: C, 35.18; H, 3.87; N, 12.82. Found: C, 35.87; H, 4.13; N, 13.07. Crystals suitable for X-ray analysis were grown by the slow vapor diffusion of diethyl ether into a solution of product in acetone.

Crystallography. All X-ray crystallographic studies were done with an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation ($\lambda(K\alpha_1)$ = 0.709 30 Å, $\lambda(K\alpha_2)$ = 0.713 59 Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental and computational procedures have been described previously.[26]

Crystals were mounted inside of thin-walled glass capillaries, which were sealed as a precaution against moisture. Data were collected with the θ–2θ scan mode for $3° \leq 2\theta_{Mo\,K\bar{\alpha}} \leq 50°$ for **1** and **2** and $3° \leq 2\theta_{Mo\,K\bar{\alpha}} \leq 46°$ for **3**. The structures were solved by Patterson and difference Fourier techniques and were refined by full-matrix least squares.[27]

X-ray Studies for $[n\text{-}BuSn(OH)(OH_2)Cl_2]_2$ (1). Crystals of **1** are fused colorless striated laths, which appear pale yellow in bulk. The crystal used for the X-ray study was cut from a larger mass and had approximate dimensions of 0.14 mm × 0.21 mm × 0.26 mm.

Crystal Data: $[n\text{-}BuSn(OH)(OH_2)Cl_2]_2$ (**1**), monoclinic space group $P2_1/n$ (alternate setting of $P2_1/c$ [C_{2h}^5–No. 14][28]), a = 6.047 (1) Å, b = 25.090 (6) Å, c = 6.556 (1) Å, β = 107.16 (1)°, Z = 2, and $\mu_{Mo\,\bar{\alpha}}$ = 3.198 mm^{-1}. A total of 1658 independent reflections ($+h,+k,\pm l$) were measured. No corrections were made for absorption.

Six of the independent non-hydrogen atoms were refined anisotropically in full-occupancy. Two sets of positions of about equal weight were found for the three terminal carbon atoms of the independent *n*-Bu group, and these six half-atoms were refined anisotropically in half-occupancy. Positions for the water and hydroxyl hydrogen atoms were obtained from a difference Fourier synthesis, and these three atoms were included in the refinement as fixed isotropic scatterers. The hydrogen atoms of the *n*-Bu groups were omitted from the refinement. The final agreement factors[29] were R = 0.037 and R_w = 0.053 for the 1413 reflections having $I \geq 2\sigma_I$.

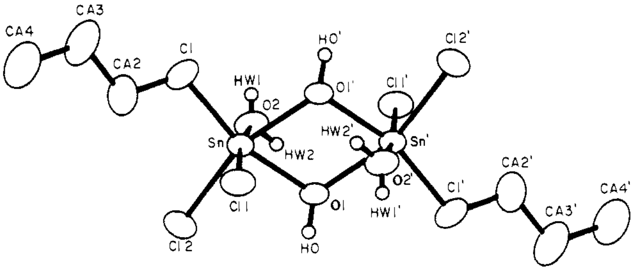

Figure 2. ORTEP plot of $[n\text{-}BuSn(OH)(OH_2)Cl_2]_2$ (**1**) with thermal ellipsoids at the 50% probability level. For purposes of clarity, only one conformation for the pendant atoms of the disordered *n*-Bu groups is chosen. Primed atoms are related to unprimed ones by $-x$, $-y$, $-z$.

Table I. Atomic Coordinates in Crystalline $[n\text{-}BuSn(OH)(OH_2)Cl_2]_2$ (**1**)[a]

atom type[b]	10^4x	10^4y	10^4z
Sn1	−850.2 (7)	644.0 (2)	348.5 (6)
Cl1	−2700 (3)	351.1 (8)	3077 (3)
Cl2	−4314 (3)	1080.5 (8)	−1820 (3)
O1	−1870 (7)	−51 (2)	−1299 (7)
O2	440 (8)	818 (2)	−2459 (7)
C1	1193 (15)	1262 (3)	2174 (12)
CA2[c]	−280 (30)	1676 (6)	2820 (23)
CA3[c]	1203 (38)	2097 (8)	4248 (32)
CA4[c]	−351 (43)	2494 (10)	5132 (41)
CB2[c]	1495 (39)	1759 (8)	1188 (31)
CB3[c]	2736 (47)	2188 (9)	2544 (44)
CB4[c]	3303 (53)	2637 (19)	1292 (63)
HO[d]	−3400	−100	−1600
HW1[d]	1600	900	−2200
HW2[d]	0	600	−3400

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 2. [c] Half-occupancy. [d] Fixed, with isotropic thermal parameter, B, fixed at 4 Å^2.

X-ray Studies for $[(C_2H_4OS)_2SnCl]_2[H][Et_4N]$ (2). The crystal used for the X-ray study was cut from a colorless polycrystalline mass and had approximate dimensions of 0.23 mm × 0.28 mm × 0.35 mm.

Crystal Data: $[(C_2H_4OS)_2SnCl]_2[H][Et_4N]$ (**2**), monoclinic space group $P2_1/n$, a = 12.522 (2) Å, b = 8.808 (1) Å, c = 26.000 (2) Å, β = 104.32 (1)°, Z = 4, and $\mu_{Mo\,K\bar{\alpha}}$ = 2.306 mm^{-1}. A total of 4875 independent reflections ($+h,+k,\pm l$) were measured. No corrections were made for absorption.

The 29 independent non-hydrogen atoms were refined anisotropically. The 24 independent methylene hydrogen atoms were included in the refinement as fixed isotropic scatterers with calculated coordinates, which were updated as refinement converged so that the final C–H bond lengths were 0.98 Å. A difference Fourier synthesis gave coordinates for the hydrogen atoms of only one methyl group (C4), and these three hydrogen atoms were included in the refinement as fixed isotropic scatterers. The H atoms of the remaining three methyl groups were omitted from the refinement. The final agreement factors[29] were R = 0.034 and R_w = 0.049 for the 4001 reflections having $I \geq 2\sigma_I$.

X-ray Studies for $[((CN)_2C_2S_2)_2SnOH]_2[Et_4N]_2$ (3). The yellow crystal used for the X-ray study was cut from a polycrystalline mass and had approximate dimensions of 0.10 mm × 0.13 mm × 0.30 mm.

Crystal Data: $[((CN)_2C_2S_2)_2SnOH]_2[Et_4N]_2$ (**3**), triclinic space group $P\bar{1}$ [C_i^1–No. 2],[30] a = 9.841 (2) Å, b = 11.201 (2) Å, c = 11.932 (2) Å, α = 65.39 (1)°, β = 76.01 (1)°, γ = 80.17 (1)°, Z = 1, and $\mu_{Mo\,K\bar{\alpha}}$ = 1.473 mm^{-1}. A total of 3206 independent reflections ($+h,\pm k,\pm l$) were measured.

A total of 23 of the independent non-hydrogen atoms were refined anisotropically in full-occupancy. Two sets of positions of about equal weight were found for the four methylene carbon atoms of the cation, and these eight half-atoms were refined anisotropically in half-occupancy. The hydroxyl hydrogen atom was located on a difference Fourier synthesis and was included in the refinement as a fixed isotropic scatterer. The remaining hydrogen atoms were omitted from the refinement. The final agreement factors[29] were R = 0.032 and R_w = 0.044 for the 2769 reflections having $I \geq 2\sigma_I$.

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(26) Sau, A. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3076–3081.

(27) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oL_p/\sigma_I$. Mean atomic scattering factors were taken from: Reference 28, 1974, Vol. IV, pp 72–98. Real and imaginary dispersion corrections for Sn, Cl, S, and O were taken from the same source, pp 149–150.

(28) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1969; Vol. I, p 99.

(29) $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

(30) Reference 28, p 75.

Table II. Selected Bond Lengths (Å) and Angles (deg) in $[n\text{-BuSn(OH)(OH}_2\text{)Cl}_2]_2$ (**1**)[a]

type[b]	length	type[b]	length
Sn–O1	2.047 (4)	Sn–Cl1	2.484 (2)
Sn–O1′	2.169 (4)	Sn–Cl2	2.419 (2)
Sn–O2	2.243 (5)	Sn–C1	2.119 (7)
type	**angle**	**type**	**angle**
O1–Sn–O1′	69.6 (2)	O1′–Sn–C1	94.2 (3)
O1–Sn–O2	81.7 (2)	O2–Sn–Cl2	83.1 (1)
O1–Sn–Cl2	90.1 (1)	O2–Sn–Cl1	171.0 (1)
O1–Sn–Cl1	89.9 (1)	O2–Sn–C1	92.0 (3)
O1–Sn–C1	162.9 (3)	Cl2–Sn–Cl1	93.52 (7)
O1′–Sn–O2	87.2 (2)	Cl2–Sn–C1	105.1 (2)
O1′–Sn–Cl2	158.7 (1)	Cl1–Sn–C1	97.0 (2)
O1′–Sn–Cl1	93.1 (1)	Sn–O1–Sn′	110.4 (2)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 2.

Table III. Atomic Coordinates in Crystalline $[(C_2H_4OS)_2SnCl]_2[H][Et_4N]$ (**2**)[a]

atom type[b]	10^4x	10^4y	10^4z
Sn1	−357.5	1691.4 (4)	1375.7 (1)
Sn2	2226.0 (3)	2665.7 (4)	1215.3 (1)
Cl1	−603 (1)	3759 (2)	1966.9 (6)
Cl2	2226 (1)	5430 (2)	1327.5 (7)
S1	−833 (1)	−330 (2)	1914.3 (6)
S2	2865 (1)	2960 (2)	405.2 (6)
S3	−1967 (1)	2386 (2)	673.4 (6)
S4	3789 (1)	2138 (2)	1952.7 (7)
O1	92 (3)	−197 (4)	931 (1)
O2	2013 (3)	325 (4)	955 (2)
O3	502 (3)	2870 (4)	896 (1)
O4	1329 (3)	1816 (4)	1753 (1)
C11	−193 (5)	−1682 (7)	1076 (3)
C12	−58 (5)	−1809 (7)	1670 (3)
C21	2249 (7)	−2 (9)	455 (3)
C22	3047 (8)	963 (10)	310 (3)
C31	−85 (6)	3296 (11)	385 (3)
C32	−1224 (7)	3605 (12)	336 (4)
C41	1910 (5)	1371 (7)	2274 (2)
C42	3039 (5)	752 (8)	2253 (2)
N	−955 (4)	1522 (5)	3626 (2)
C1	−853 (6)	1624 (9)	4219 (3)
C2	342 (7)	1696 (11)	4567 (3)
C3	−2175 (5)	1527 (8)	3356 (2)
C4	−2459 (6)	1478 (9)	2757 (3)
C5	−431 (5)	33 (9)	3495 (3)
C6	−950 (6)	−1386 (8)	3632 (4)
C7	−358 (6)	2804 (9)	3436 (3)
C8	−791 (8)	4379 (9)	3547 (4)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 4.

Table IV. Selected Bond Lengths (Å) and Angles (deg) in $[(C_2H_4OS)_2SnCl]_2[H][Et_4N]$ (2)[a]

type[b]	length	type[b]	length
Sn1–O1	2.178 (4)	Sn2–O2	2.165 (4)
Sn1–O3	2.111 (3)	Sn2–O3	2.121 (3)
Sn1–O4	2.100 (3)	Sn2–O4	2.133 (3)
Sn1–S1	2.428 (2)	Sn2–S2	2.445 (2)
Sn1–S3	2.439 (2)	Sn2–S4	2.422 (2)
Sn1–Cl1	2.451 (2)	Sn2–Cl2	2.452 (2)
O1–O2	2.435 (5)		
type	**angle**	**type**	**angle**
Cl1–Sn1–S1	95.53 (5)	Cl2–Sn2–S4	96.90 (6)
Cl1–Sn1–O1	171.7 (1)	Cl2–Sn2–O2	168.2 (1)
Cl1–Sn1–O3	99.6 (1)	Cl2–Sn2–O3	86.1 (1)
Cl1–Sn1–O4	97.5 (1)	Cl2–Sn2–O4	104.8 (1)
Cl1–Sn1–S3	94.25 (6)	Cl2–Sn2–S2	90.39 (6)
S1–Sn1–O1	83.0 (1)	S4–Sn2–O2	94.4 (1)
S1–Sn1–O3	159.2 (1)	S4–Sn2–O3	150.6 (1)
S1–Sn1–O4	97.5 (1)	S4–Sn2–O4	82.4 (1)
S1–Sn1–S3	109.90 (6)	S4–Sn2–S2	109.27 (6)
O1–Sn1–O3	79.9 (1)	O2–Sn2–O3	85.6 (1)
O1–Sn1–O4	85.7 (1)	O2–Sn2–O4	80.0 (1)
O1–Sn1–S3	93.9 (1)	O2–Sn2–S2	82.7 (1)
O3–Sn1–O4	69.5 (1)	O3–Sn2–O4	68.7 (1)
O3–Sn1–S3	83.2 (1)	O3–Sn2–S4	150.6 (1)
O4–Sn–S3	152.4 (1)	O4–Sn2–S4	82.4 (1)
Sn1–S1–C12	95.5 (2)	Sn2–S2–C22	95.4 (2)
Sn1–O1–C11	116.3 (3)	Sn2–O2–C21	116.0 (4)
Sn1–O3–Sn2	110.2 (2)	Sn2–S4–C42	93.8 (2)
Sn1–O3–C31	117.9 (4)	Sn1–O4–Sn2	110.1 (1)
Sn2–O3–C31	129.7 (4)	Sn1–O4–C41	130.3 (3)
Sn1–S3–C32	94.8 (3)	Sn2–O4–C41	119.5 (3)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 4.

Table V. Atomic Coordinates in Crystalline $[((CN)_2C_2S_2)_2SnOH]_2[Et_4N]_2$ (3)[a]

atom type[b]	10^4x	10^4y	10^4z
Sn	954.0 (3)	1306.7 (3)	380.1 (3)
S1	518 (2)	2365 (1)	−2573 (1)
S2	61 (2)	3483 (1)	−246 (1)
S3	1565 (1)	346 (1)	1758 (1)
S4	3528 (1)	1586 (1)	−1208 (1)
O	−1057 (3)	552 (3)	486 (3)
N5	2158 (9)	−4707 (8)	4144 (8)
N6	2732 (8)	−5984 (7)	1421 (8)
N7	4159 (7)	805 (6)	3199 (5)
N8	6419 (5)	2200 (5)	−122 (5)
C1	−657 (6)	3659 (5)	−2420 (5)
C2	−854 (6)	4113 (5)	−1472 (6)
C3	3207 (5)	959 (5)	1329 (5)
C4	3988 (5)	1431 (5)	163 (5)
C5	1489 (8)	−4260 (7)	3377 (7)
C6	1916 (7)	−5157 (6)	1452 (7)
C7	3746 (6)	890 (6)	2356 (5)
C8	5334 (5)	1869 (5)	9 (5)
N1	−2929 (5)	2683 (5)	3712 (4)
C9A[c]	−2492 (10)	1848 (9)	2885 (8)
C9B[c]	−3021 (63)	1265 (33)	4221 (34)
C10	−2335 (9)	389 (8)	3584 (9)
C11A[c]	−4433 (9)	2384 (8)	4424 (8)
C11B[c]	−3623 (63)	3142 (33)	4814 (34)
C12	−5047 (10)	3082 (9)	5282 (9)
C13A[c]	−1946 (10)	2257 (11)	4686 (9)
C13B[c]	−1410 (49)	3254 (49)	3268 (38)
C14	−418 (10)	2383 (10)	4140 (10)
C15A[c]	−2796 (13)	4099 (10)	2851 (10)
C15B[c]	−3714 (35)	3510 (35)	2501 (30)
C16	−3846 (11)	4699 (9)	1966 (10)
H[d]	−1750	1250	100

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 5. [c] Half-occupancy. [d] Fixed, with B fixed at 5 Å^2.

Results

The atom-labeling scheme for **1** is given in the ORTEP plot of Figure 2. Atomic coordinates are given in Table I, and selected bond lengths and angles are given in Table II. The Corresponding information for **2** and **3** is given in the ORTEP plots of Figures 4 and 5 and in Tables III–VI. Thermal parameters, hydrogen atom parameters, and additional bond lengths and angles are provided as supplementary material.

Discussion

Syntheses. Dimeric structures containing the distannoxane ring, Sn_2O_2, with an octahedral arrangement of ligand atoms about tin(IV) are known for $[SnCl_3(OH)(OH_2)]_2 \cdot 3C_4H_8O_2$[31] and $[SnCl_3(OCH_3)(CH_3OH)]_2$.[32] The latter substance forms in high yield on reacting tin tetrachloride in benzene with a methanol solution of sodium methoxide (eq 1). The former substance forms,

$$SnCl_4 + Na(OMe) + MeOH \rightarrow {}^1/_2[SnCl_3(OMe)(MeOH)]_2 + NaCl \quad (1)$$

despite precautions to exclude moisture,[31] from the oxidation of the complex $SnCl_2 \cdot C_4H_8O_2$ in an attempted recrystallization in dioxane solution at room temperature (eq 2). These distannates

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(31) Bokii, N. G.; Struchkov, Y. T. *Zh. Strukt. Khim.* **1971**, *12*, 253–256.

(32) Sterr, G.; Mattes, R. *Z. Anorg. Allg. Chem.* **1963**, *322*, 319–325.

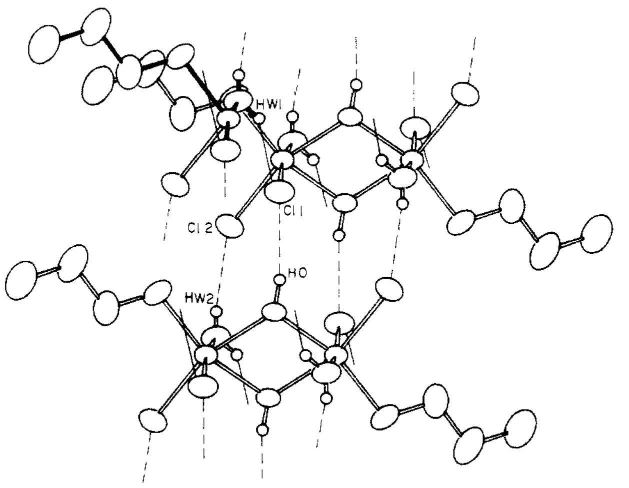

Figure 3. ORTEP plot showing the propagation of the three independent intermolecular hydrogen-bonding interactions in $[n\text{-BuSn(OH)(OH}_2)\text{Cl}_2]_2$ (**1**). Two complete molecules, which are translationally related along $\vec{a}$, and a portion of a molecule, which is translationally related along $\vec{c}$ (shaded bonds), are shown. Hydrogen bonds forming chains along $\vec{a}$ are shown as dashed lines. Hydrogen bonds forming chains along $\vec{c}$ are shown as narrow solid lines.

Table VI. Selected Bond Lengths (Å) and Angles (deg) in $[((CN)_2C_2S_2)_2SnOH]_2[Et_4N]_2$ (**3**)[a]

type[b]	length	type[b]	length
Sn-O	2.134 (3)	Sn-S3	2.502 (1)
Sn-O′	2.122 (3)	Sn-S4	2.509 (1)
Sn-S1	2.494 (1)	S1-C1	1.737 (6)
Sn-S2	2.503 (1)	S2-C2	1.735 (6)
S4-C4	1.734 (5)	S3-C3	1.741 (5)
type	**angle**	**type**	**angle**
O-Sn-S1	96.68 (9)	S2-Sn-S4	101.84 (5)
O-Sn-S2	91.66 (9)	S2-Sn-O′	162.54 (9)
O-Sn-S3	87.83 (9)	S3-Sn-S4	86.10 (5)
O-Sn-S4	165.46 (9)	S3-Sn-O′	93.9 (1)
O-Sn-O′	72.7 (1)	S4-Sn-O′	94.59 (9)
S1-Sn-S2	85.84 (5)	Sn-S1-C1	98.2 (2)
S1-Sn-S3	175.37 (5)	Sn-S2-C2	98.4 (2)
S1-Sn-S4	89.73 (5)	Sn-S3-C3	97.7 (2)
S1-Sn-O′	88.38 (9)	Sn-S4-C4	98.0 (2)
S2-Sn-S3	93.04 (5)	Sn-O-Sn′	107.3 (1)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 5.

have X-ray structures similar to that shown schematically in Figure 1a.

$$3SnCl_2{\cdot}C_4H_8O_2 + 4H_2O \xrightarrow{\text{alcohol}} [SnCl_3(OH)(OH_2)]_2{\cdot}3C_4H_8O_2 + Sn + H_2 \quad (2)$$

The formation of **2** and **3** also proceeds by a hydrolysis pathway, yielding the distannoxane ring system. These derivatives provide the first examples of this class where cyclic ligands are incorporated. The unsaturated ring derivative **3** is fully cyclized while a Sn-Cl bond remains intact in **2** made up of saturated ring ligands. The reaction leading to the mercaptoethanolate **2** is expressed in eq 3 and that for the dicyanoethylenedithiolate **3** is given in eq 4.

$$2SnCl_4{\cdot}5H_2O + 4Na_2[SCH_2CH_2O] + Et_4NCl \rightarrow \underset{\mathbf{2}}{[(C_2H_4OS)_2SnCl]_2[H][Et_4N]} + 7NaCl + NaOH + 9H_2O \quad (3)$$

$$SnCl_4{\cdot}5H_2O + 2Na_2[(CN)_2C_2S_2] + Et_4NCl \rightarrow {}^1/_2[\underset{\mathbf{3}}{[((CN)_2C_2S_2)_2SnOH]_2[Et_4N]_2}] + 4NaCl + HCl + 4H_2O \quad (4)$$

In view of our work[1b] showing that the relatively unstable five-coordinated fluorine-containing bis(mercaptophenolate) **4** undergoes hydrolysis to the six-coordinated tris(stannate) **5** with accompanying cleavage of the tin-fluorine bond (eq 5), formation

$$\underset{\mathbf{4}}{3[(C_6H_4OS)_2SnF][Et_4N]} + 2H_2O \rightarrow [(C_6H_4OS)_3Sn]_2[H]_3[Et_4N] + 2Et_4NF + SnO_2 + HF \quad (5)$$

of an analogous five-coordinated chlorine-containing intermediate, **6**, is suggested in the synthesis of **3** (eq 6). Subsequent hydrolysis

$$SnCl_4{\cdot}5H_2O + 2Na_2[(CN)_2C_2S_2] + Et_4NCl \rightarrow \underset{\mathbf{6}}{[((CN)_2C_2S_2)_2SnCl][Et_4N]} + 4NaCl \quad (6)$$

then gives the distannoxane product **3** (eq 7). An analogous

$$\mathbf{6} + H_2O \rightarrow {}^1/_2\mathbf{3} + HCl \quad (7)$$

five-coordinated intermediate, **7**, appearing in the synthesis of the distannate **2** is reasonable (eq 8). However, unlike the reaction

$$2SnCl_4{\cdot}5H_2O + 4Na_2[SCH_2CH_2O] + Et_4NCl \rightarrow \underset{\mathbf{7}}{[(SCH_2CH_2O)_2SnCl]_2[Et_4N][Na]} + 7NaCl + 5H_2O \quad (8)$$

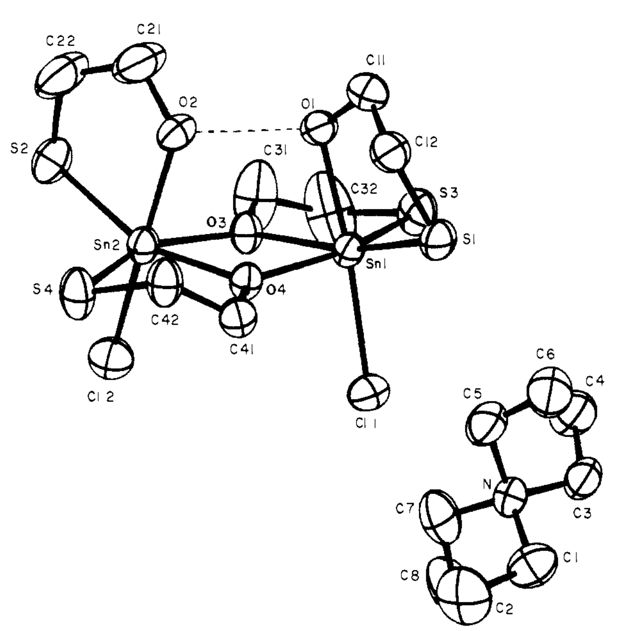

Figure 4. ORTEP plot of $[(C_2H_4OS)_2SnCl]_2[H][Et_4N]$ (**2**) with thermal ellipsoids at the 50% probability level. The interaction of the proton with O1 and O2 is indicated by a dashed line. Hydrogen atoms are omitted for purposes of clarity.

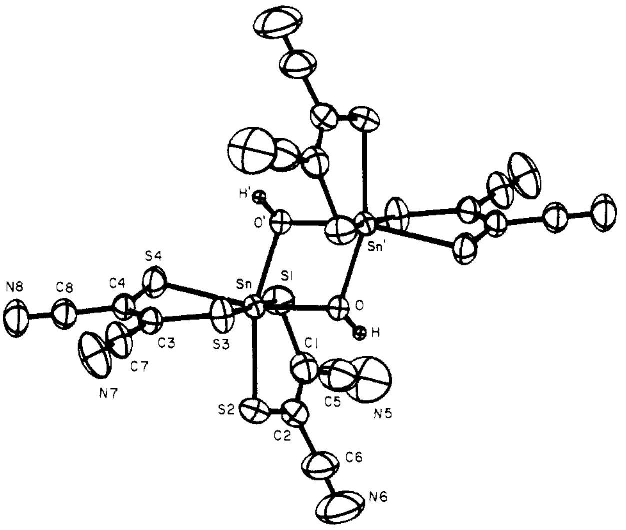

Figure 5. ORTEP plot of the anion of $[((CN)_2C_2S_2)_2SnOH]_2[Et_4N]_2$ (**3**) with thermal ellipsoids at the 50% probability level. Primed atoms are related to unprimed ones by $-x$, $-y$, $-z$.

Table VII. Bond Lengths (Å) and Interbond Angles (deg) for Hexacoordinated Tin(IV) Derivatives with Distannoxane Rings

		bond length		angle[a]		
no.	compound	Sn–Cl	Sn–O (av)[a]	O–Sn–O	Sn–O–Sn	ref
1	$[n\text{-BuSn(OH)(OH}_2)\text{Cl}_2]_2$	2.296 (2) av	2.108 (4) av	69.6 (2)	110.4 (2)	this work
2	$[(\text{SCH}_2\text{CH}_2\text{O})_2\text{SnCl}]_2[\text{H}][\text{Et}_4\text{N}]$	2.451 (2)	2.116 (3)	69.1 (1) av	110.2 (2) av	this work
3	$[((\text{CN})_2\text{C}_2\text{S}_2)_2\text{SnOH}]_2[\text{Et}_4\text{N}]_2$		2.128 (3)	72.7 (1)	107.3 (1)	this work
4	$[\text{EtSn(OH)(OH}_2)\text{Cl}_2]_2$	2.423 (8) av	2.110 (11)	70.9 (6)	109.1 (7)	16
5	$[\text{SnCl}_3(\text{OH})(\text{OH}_2)]_2\cdot 3\text{C}_4\text{H}_8\text{O}_2$	2.37 (2) av	2.07 (3)	69.2 (1.3)	110.8 (1.6)	31
6	$[\text{PhSn(O)O}_2\text{CC}_6\text{H}_{11}]_6$[b]		2.106 (3)	78.0 (1) av	99.8 (1) av	17

[a] The Sn–O bond parameters refer to those in the Sn_2O_2 unit. [b] Other members of this drum class[17–19] and related open-drum class[18–19] have similar Sn_2O_2 bond parameters.

yielding **3**, the hydrolysis step here to give **2** does not result in rupture of the Sn–Cl bond (eq 9). The retention of the latter

$$\mathbf{7} + H_2O \rightarrow \mathbf{2} + NaOH \qquad (9)$$

Sn–Cl bond may be influenced by the presence of the less electron-withdrawing saturated ring ligands in **2** compared to the unsaturated ring system in **3**. Also, the availability of a ring oxygen atom for coordination to form the distannoxane system relative to the presence of only sulfur atoms in **3** may be influential in allowing Sn–Cl bond retention.

In the pathways leading to both **2** and **3**, it is seen that the Sn–S bonds maintain their integrity as the stannoxane ring systems form in the hydrolysis processes. The accompanying attainment of six-coordination for tin is in agreement with our previous results,[1b,23,24] which show that Sn–O bonds are almost nonexistent for five-coordinated anionic tin, despite attempts to form them, but are conducive in stabilizing tin(IV) in more highly coordinated environments.

The hydrolysis of n-$BuSnCl_3$ results in the neutral dihydroxydistannate derivative **1**, which exists as a six-coordinated species rather than a five-coordinated one due to ligation of water molecules. The structure of **1** is very similar to that of the related ethyl compound $[EtSn(OH)(OH_2)Cl_2]_2$.[16] In contrast, hydrolysis of di-*tert*-butyltin dichloride gives a neutral distannate having five-coordinated tin atoms, $[(t\text{-Bu})_2Sn(OH)Cl]_2$.[33] Introduction of two alkyl groups compared to one serves to decrease the acidity of tin. As a consequence, further coordination is rendered less likely. This situation corresponds to that found in the tetraorganodistannoxanes, $[XR_2SnOSnR_2X]_2$, discussed in the introduction. All of these dimeric compositions exhibit pentacoordination.

NMR Data. Blunden, Smith, and Gillies[15] have recorded the ^{119}Sn NMR of $MeSnCl_3$ in D_2O and have found evidence for the presence of a variety of hydrolysis products, $MeSn(OH)Cl_2\cdot 2H_2O$, $MeSn(OH)_2Cl\cdot nH_2O$, and $[MeSn(OH)(H_2O)_4]^{2+}$, successively indicating the replacement of additional chlorine atoms. For n-$BuSn(OH)(OH_2)Cl_2$ (**1**), they have recorded the ^{119}Sn spectrum in D_2O and found these resonances; −283, −503, and −536 ppm. On recording the spectrum in acetone-d_6, we observed only one major peak of −408.6 ppm. This chemical shift is consistent with six-coordinated tin and suggests that the dimeric structure $[n\text{-BuSn(OH)(OH}_2)Cl_2]_2$ (1) is retained in solution. Presumably, the signals at −503 and −536 ppm observed by Blunden et al.[15] are a result of further hydrolysis.

Structural Details. All three compounds exist in the solid state as hexacoordinated tin dimers in which the four Sn–O bonds are of comparable length. The anions in **1** and **3** have C_i symmetry, with the halves of the dimers related by a crystallographic inversion center located in the center of the four-membered $(SnO)_2$ ring. The anion in **2** has no crystallographic symmetry, but for the idealized molecular symmetry, C_2, the halves of the dimer would be related by a 2-fold axis passing through the center of the four-membered ring.

In **2**, for purposes of electrical neutrality, two cations are required for each binuclear tin species. The X-ray results showed only one Et_4N^+ cation for each binuclear species and gave no indication of possible protonated oxygen atoms. The surprisingly short intramolecular distance between O1 and O2 of 2.435 (5) Å is less than the van der Waals sum of 2.8 Å and is comparable to the O–O distances found for the very short O–H–O bonds in acid salts of carboxylic acids, which are believed to be symmetric.[34] It seems reasonable to conclude that the proton that is required to maintain electrical neutrality is involved in a strong and possibly symmetric hydrogen-bonding interaction with O1 and O2. In the event that the hydrogen atom is truly centered between O1 and O2, it would lie on the 2-fold axis if the idealized C_2 symmetry were realized. Such symmetry is believed to favor the formation of symmetric hydrogen bonds.[34]

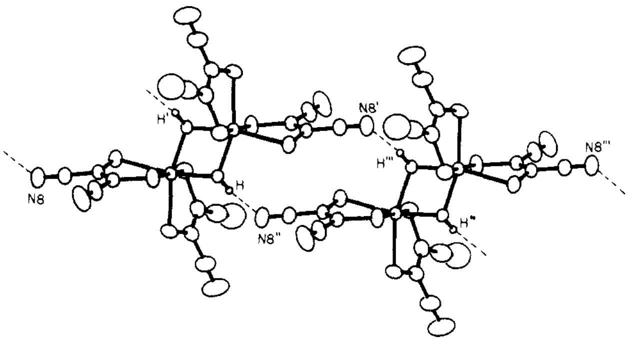

Figure 6. ORTEP plot showing the propagation of the hydrogen-bonded chain along $\vec{a}$ in $[((CN)_2C_2S_2)_2SnOH]_2[Et_4N]_2$ (**3**). Hydrogen bonds are shown as dashed lines. Symmetry operators are the following: primed values = $-x, -y, -z$; double-primed values = $x - 1, y, z$; triple-primed values = $-x - 1, -y, -z$.

For compounds **1** and **3**, there is intermolecular hydrogen bonding in the lattices. In **1**, the water hydrogen atoms and the hydroxyl hydrogen atoms are each involved in a single hydrogen bond to chlorine atoms of translationally related molecules. The pertinent distances are HO–Cl1 = 2.36 Å, HW1–Cl1 = 2.48 Å, and HW2–Cl2 = 2.45 Å. As shown in Figure 3, these interactions generate hydrogen-bonded chains of molecules in the *a* and *c* directions.

In **3**, there are hydrogen bonds between the hydroxyl hydrogen atoms and nitrogen atoms N8 of translationally related molecules. The pertinent distance is H–N8 = 1.946 Å. The propagation of hydrogen-bonded chains along *a* is shown in Figure 6.

Summarized in Table VII is a comparison of bond parameters of related hexacoordinated tin(IV) compounds that have the distannoxane ring system. The range of Sn–O bond lengths over this series, discounting the lower resolution study of the dioxane solvate,[31] is surprisingly narrow, 2.11–2.13 Å, and coincides with the single-bond covalent radius value of 2.13 Å.[35] The lengths of the Sn–Cl bonds assume considerably more variability. They cover the range 2.30–2.45 Å. The Sn–O–Sn and O–Sn–O bond angles are reasonably close to one another for the entries other than that for the drum structure, $[PhSn(O)O_2CC_6H_{11}]_6$.[17] Here, six Sn_2O_2 ring untis are linked together and form the sides of the drum while the other compounds have only one such unit. Wrapping these units around to form the drum presumably is

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(33) Johnson, S. E.; Day, R. O.; Holmes, J. M., unpublished work.

(34) Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solids*; Benjamin: New York, 1968; p 181.

(35) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper & Row: New York, 1983; p 258.

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responsible for the difference in bond angles between it and the other more related derivatives.

Acknowledgment. The support of this research by the National Science Foundation (Grant CHE8504737) is gratefully acknowledged. We also thank the University of Massachusetts Computing Center for generous allocation of computer time.

Supplementary Material Available: Thermal parameters and additional bond lengths and angles (Tables S1 and S2, respectively, for **1**, Tables S3 and S5 for **2**, Tables S6 and S7 for **3**) and fixed hydrogen atom parameters for **2** (Table S4) (8 pages); listings of calculated and observed structure factor amplitudes for **1–3** (32 pages). Ordering information is given on any current masthead page.

Photoinduced Intramolecular Electron Transfer in Peptide-Bridged Molecules

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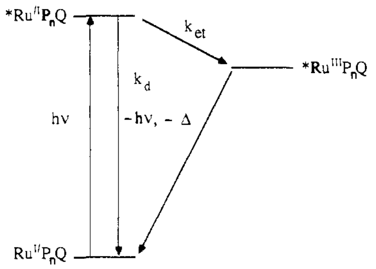
Abstract: Two series of molecules have been prepared and characterized in which a polypyridyl Ru(II) complex is linked to *p*-dimethoxybenzene (DMB) and *p*-benzoquinone (Q) moieties by peptide bridges containing the amino acid L-proline (Pro). The photophysical properties of the metal-to-ligand charge transfer (MLCT) excited state of the Ru(II) chromophore have been examined for the complexes with 0, 1, 2, 3, and 4 intervening Pro residues. Steady state and time resolved luminescence experiments on the Pro-bridged DMB system show that the properties of the Ru MLCT excited state are only slightly modified from those of an unsubstituted model complex by the presence of covalently attached DMB peptides. Experiments on the Pro-bridged Ru–Q complexes show that the Q site quenches the yield and lifetime of the Ru MLCT emission. Furthermore, the quenching efficiency is diminished as the number of peptide spacers is increased. The quenching process is ascribed to long-range intramolecular Ru-to-Q electron transfer. This hypothesis is supported by time-resolved luminescence data which suggest that the average electron transfer rate falls sharply with an increase in the peptide bridge length.

There has been considerable interest recently in exploring the role of distance in the rate of electron transfer between donor and acceptor sites that are spatially separated.[2] Studies involving various chemical and physical approaches have addressed this important problem. Rates have been measured for electron transfer between donor and acceptor sites that are randomly distributed in glassy matrices,[3–5] held at fixed distances by protein frameworks[4c,6–8] or between sites that are separated by peptide oligomers,[10] rigid carbon–carbon bond frameworks,[11–16] or by various aliphatic[17,18] and aromatic spacers.[19] Several goals are

Scheme I



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(2) For reviews, see: (a) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265–322. (b) Newton, M. D.; Sutin, N. *Annu. Rev. Phys. Chem.* **1984**, *35*, 437–480. (c) De Vault, D. *Quantum-Mechanical Tunnelling in Biological Systems*; 2nd ed.; Cambridge University Press: New York, 1984.

(3) (a) Beitz, J. V.; Miller, J. R. *J. Chem. Phys.* **1979**, *71*, 4579–4595. (b) Miller, J. R.; Beitz, J. V. *J. Chem. Phys.* **1981**, *74*, 6746–6756. (c) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. *J. Am. Chem. Soc.* **1984**, *106*, 5057–5068. (d) Miller, J. R.; Hartman, K. R.; Abrash, S. *J. Am. Chem. Soc.* **1982**, *104*, 4296–4298.

(4) (a) Strauch, S.; McLendon, G.; McGuire, M.; Guarr, T. *J. Phys. Chem.* **1983**, *87*, 3579–3581. (b) Guarr, T.; McGuire, M.; McLendon, G. *J. Am. Chem. Soc.* **1985**, *107*, 5104–5111. (c) McLendon, G.; Guarr, T.; McGuire, M.; Simolo, K.; Strauch, S.; Taylor, K. *Coord. Chem. Rev.* **1985**, *64*, 113–124.

(5) Domingue, R. P.; Fayer, M. D. *J. Chem. Phys.* **1985**, *83*, 2242–2251.

(6) (a) Winkler, J. R.; Nocera, D. G.; Yocum, K. M.; Bordignon, E.; Gray, H. B. *J. Am. Chem. Soc.* **1982**, *104*, 5798–5800. (b) Nocera, D. G.; Winkler, J. R.; Yocum, K. M.; Bordignon, E.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 5145–5150. (c) Crutchley, R. J.; Ellis, W. R., Jr.; Gray, H. B. *J. Am. Chem. Soc.* **1985**, *107*, 5002–5004. (d) Kostic, N. M.; Margalit, R.; Che, C.-M.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 7765–7767. (e) Mayo, S. L.; Ellis, W. R., Jr.; Crutchley, R. J.; Gray, H. B. *Science* **1986**, *233*, 948–952.

(7) (a) McGourty, J. L.; Blough, N. V.; Hoffman, B. M. *J. Am. Chem. Soc.* **1983**, *105*, 4470–4472. (b) Peterson-Kennedy, S. E.; McGourty, J. L.; Hoffman, B. M. *J. Am. Chem. Soc.* **1984**, *106*, 5010–5012. (c) Peterson-Kennedy, S. E.; McGourty, J. L.; Ho, P. S.; Sutoris, C. J.; Liang, N.; Zemel, H.; Blough, N. V.; Margoliash, E.; Hoffman, B. M. *Coord. Chem. Rev.* **1985**, *64*, 125–133.

(8) (a) McLendon, G. L.; Winkler, J. R.; Nocera, D. G.; Mauk, M. R.; Mauk, A. G.; Gray, H. B. *J. Am. Chem. Soc.* **1985**, *107*, 739–740. (b) McLendon, G.; Miller, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 7811–7816. (c) Simolo, K. P.; McLendon, G. L.; Mauk, M. R.; Mauk, A. G. *J. Am. Chem. Soc.* **1984**, *106*, 5012–5013.

(9) (a) Isied, S. S.; Kuehn, C.; Worosila, G. *J. Am. Chem. Soc.* **1984**, *106*, 1722–1726.

(10) (a) Isied, S. S.; Vassilian, A. *J. Am. Chem. Soc.* **1984**, *106*, 1726–1732. (b) Isied, S. S.; Vassilian, A. *J. Am. Chem. Soc.* **1984**, *106*, 1732–1736. (c) Isied, S. S.; Vassilian, A.; Magnuson, R. H.; Schwartz, H. A. *J. Am. Chem. Soc.* **1985**, *107*, 7432–7438.

(11) (a) Calcaterra, L. T.; Closs, G. L.; Miller, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 670–671. (b) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047–3049. (c) Closs, G. L.; Calcaterra, L. T.; Green, N. J.; Penfield, K. W.; Miller, J. R. *J. Phys. Chem.* **1986**, *90*, 3673–3683. (d) Penfield, K. W.; Miller, J. R.; Paddon-Row, M. N.; Cotsaris, E.; Oliver, A. M; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 5061–5065.

(12) (a) Pasman, P.; Koper, N. W.; Verhoeven, J. W. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 363–364. (b) Pasman, P.; Mes, G. F.; Koper, N. W.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1985**, *107*, 5839–5843.

(13) (a) Wasielewski, M. R.; Niemczyk, M. P. *J. Am. Chem. Soc.* **1984**, *106*, 5043–5045. (b) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 1080–1082. (c) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 5562–5563.

(14) (a) Hush, N. S. *Coord. Chem. Rev.* **1985**, *64*, 135–157. (b) Oevering, H.; Paddon-Row, M. N.; Heppener, M.; Oliver, A. M.; Cotsaris, E.; Verhoeven, J. W.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 3258–3269.

(15) (a) Joran, A. D.; Leland, B. A.; Geller, G. G.; Hopfield, J. J.; Dervan, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 6090–6092. (b) Leland, B. A.; Joran, A. D.; Felker, P. M.; Hopfield, J. J.; Zewail, A. H.; Dervan, P. B. *J. Phys. Chem.* **1985**, *89*, 5571–5573.