ORGANOMETALLICS

Volume 4, Number 12, December 1985

Organogermanium(IV), -tin(IV), and -lead(IV) Esters of Tetramethylenedithiocarbamic Acid. The Crystal and Molecular Structure of (Tetramethylenedithiocarbamato)triphenyltin(IV) and -lead(IV)†

E. M. Holt

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078

F. A. K. Nasser, A. Wilson, Jr., and J. J. Zuckerman*

Department of Chemistry, University of Oklahoma, Norman, Oklahoma 73019

Received October 16, 1984

Eight organo group 14 esters of tetramethylenedithiocarbamic acid, $R_nE(S_2CNC_4H_5)_{4-n}$ where E = Ge, $n = 3$, and R = C_2H_5, E = Sn, $n = 2$, and R = CH_3, C_2H_5, n-C_4H_9, n-C_8H_{17}, and C_6H_5, E = Sn, $n = 3$, and R = n-C_4H_9 and C_6H_5 (I), and E = Pb, $n = 3$, and R = C_6H_5 (II), have been synthesized from the ammonium salt of the carbamic acid and the group 14 chloride in methanol or chloroform and characterized by elemental analyses, physical properties, and infrared, Raman, mass, and, for the tin compounds, ^{119m}Sn Mössbauer spectroscopies. The crystal and molecular structures of two isomorphous examples (tetramethylenedithiocarbamato)triphenyltin(IV) (I) and -lead(IV) (II) were determined. I: mp 170–173 °C, $C_{23}H_{23}NS_2Sn$, crystallizes in the space group *Pcab* with $a = 23.784$ (12) Å, $b = 16.408$ (5) Å, $c = 11.346$ (4) Å, $V = 4427.8$ (30) Å^3, $\alpha = \beta = \gamma = 90.0°$, $Z = 8$, $\rho_{calcd} = 1.488$ g cm^{-3}. II: mp 166–168 °C, $C_{23}H_{23}NPbS_2$, is isomorphous with $a = 11.360$ (3) Å, $b = 23.593$ (10) Å, $c = 16.558$ (4) Å, $V = 4437.9$ (25) Å^3, $Z = 8$, $\rho_{calcd} = 1.750$ g cm^{-3}. The structures were solved from 2669 and 1720 data points, respectively, measured by ambient temperatures with monochromatic Mo Kα radiation ($\lambda = 0.71069$ Å), and refined to final R values of 5.3 (I) and 8.3% (II). The monodentate ligands give distorted T_d symmetry at each metal center with bonded d(M–S) of 2.468 (3) and 2.56 (1) Å vs. nonbonded d(M···S) of 3.106 (3) and 3.26 (1) Å, respectively, for I and II.

Our investigations of the oxy- and thiophosphorus acid derivatives of tin(IV) taught that substitution changes on the oxygen atoms remote from the metal–sulfur bonds could determine the coordination number and direct the choice of geometry at the metal center.[1] For example, in the diphenyltin(IV) derivatives, changing the *O,O'*-diethyl to the diisopropyl analogue converts the anisobidentate chelate of the former ($<$C—Sn—*C* = 135°) with distinct P=S and P—S bonds[2] to a centrosymmetric isobidentate chelate ($<$C—Sn—C = 180° by symmetry) with equal P—Sn and S—P bonds. An additional difference is that while the molecules of the diethyl derivative pack with no apparent interaction into the unit cell, the diisopropyl molecules pack along the crystallographic *c* axis to produce an Sn–Sn array at a relatively short distance (6.341 Å). Indeed, this compound behaves as a "virtual polymer" owing to its tightly packed lattice along this axis.[3] For the triphenyltin(IV) derivative, the analogue of the title compounds described here, *O,O'*-diethyl substitution produces a four-coordinated situation at the tin(IV) atom[4] with a rare monodentate dithiophosphate ligand (only one other example is known[5]). In this paper we report the structures of the tin and lead dithiocarbamate analogues

---

† In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of the wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

(1) Molloy, K. C.; Zuckerman, J. J. *Acc. Chem. Res.* **1983**, *16*, 386.

(2) Lieblich, B. W.; Tomassini, M. *Acta Crystallogr., Sect B: Struc. Crystallogr. Cryst. Chem.* **1978**, *B34*, 944.

(3) Molloy, K. D.; Hossain, M. B.; van der Helm, D.; Zuckerman, J. J.; Haiduc, I. *Inorg. Chem.* **1980**, *19*, 2041.

(4) Molloy, K. C.; Hossain, M. B.; van der Helm, D.; Zuckerman, J. J.; Haiduc, I. *Inorg. Chem.* **1979**, *18*, 3507.

(5) Shetty, P. S.; Fernando, Q. J. *J. Am. Chem. Soc.* **1970**, *92*, 3964.

Table I. Physical Data, Analysis, and Yields for the $R_nM[S_2CN(CH_2)_4]_{4-n}$ (n = 2, 3) (Me = Ge, Sn, Pb) Derivatives

compd	mp, °C	C found	C calcd	H found	H calcd	yields, %
$(C_2H_5)_3GeL$	oil	42.99	43.19	7.39	7.53	52
$(CH_3)_2SnL_2$[a,b]	231–234	32.45	32.68	5.07	5.00	62
$(C_2H_5)_2SnL_2$	211–213	35.57	35.84	5.66	5.55	77
$(n\text{-}C_4H_9)_2SnL_2$[b]	92–94	40.97	41.17	6.50	6.48	76
$(n\text{-}C_8H_{17})_2SnL_2$	oil	48.79	49.00	7.75	7.85	62
$(C_6H_5)_2SnL_2$	219–221	46.56	46.75	4.65	4.60	75
$(C_6H_5)_3SnL$ (I)	170–173	55.66	55.68	4.64	4.64	72
$(C_6H_5)_3PbL$ (II)	166–168	43.13	43.19	7.4	7.53	52

[a] L = $S_2CN(CH_2)_4$. [b] Reported in ref 10 and 11, but no melting points given.

of the even less sterically demanding 1-pyrrolidine substituent.

Experimental Section

Organotin, -lead, and germanium starting materials and tetramethylenedithiocarbamic acid ammonium salt were of commercial grade and were used without further purification. Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Infrared spectra were recorded on a Beckman 4250 spectrometer as Nujol mulls on CsI plates. Mass spectra were recorded on a Hewlett-Packard 5985B mass spectrometer at an exciting voltage of 70 eV. Raman data were recorded on a Spex Ramalog 5 laser Raman spectrometer. All solid products were recrystallized from chloroform. The compounds studied are listed in their yields, melting points, and microanalytical data in Table I.

(Tetramethylenedithiocarbamato)triethylgermane(IV), $(C_2H_5)_3GeS_2CN(CH_2)_4$. To a methanol solution (150 mL) of ammonium tetramethylenedithiocarbamate (0.82 g, 5.0 mmole was added triethylchlorogermane (0.11 g, 5.0 mmol). The mixture was refluxed for 3 h, the precipitated ammonium chloride removed by filtration, and excess solvent removed under reduced pressure, yielding a pale oil (0.479, 51%).

Bis(tetramethylenethiocarbamato)dimethyltin(IV), $(CH_3)_2Sn[S_2CN(CH_2)_4]_2$. To a methanol solution (150 mL) of ammonium tetramethylenedithiocarbamate (3.20 g, 10.0 mmol) was added dimethyltin(IV) dichloride (2.19 g, 10.0 mmol). The mixture was refluxed for 3 h and the precipitated ammonium chloride removed by filtration. The filtrate, after cooling overnight, gave the product as colorless crystals (3.40 g, 62%).

Bis(tetramethylenedithiocarbamato)diethyltin(IV), $(C_2H_5)_2Sn[S_2CN(CH_2)_4]_2$. To a methanol solution (150 mL) of ammonium tetramethylenedithiocarbamate (1.64 g, 5.00 mmol) was added diethyltin(IV) dichloride (1.24 g, 5.00 mmol). The mixture was refluxed for 3 h, the precipitated ammonium chloride was removed by filtration, and excess solvent was removed under reduced pressure, yielding colorless crystals (2.21, 77%).

Bis(tetramethylenedithiocarbamato)di-*n*-dibutyltin(IV), $(n\text{-}C_4H_9)_2Sn[S_2CN(CH_2)_4]_2$. To a methanol solution (150 mL) of ammonium tetramethylenedithiocarbamate (1.64 g, 5.0 mmol) was added dibutyltin(IV) dichloride (1.52 g, 5.00 mmol). The mixture was refluxed for 3 h, the precipitated ammonium chloride was removed by filtration, and excess solvent was removed under reduced pressure, yielding a white powder (2.40 g, 76%).

Bis(tetramethylenedithiocarbamato)di-*n*-octyltin(IV), $(n\text{-}C_8H_{17})_2Sn[S_2CN(CH_2)_4]_2$. To a methanol solution (150 mL) of ammonium tetramethylenedithiocarbamate (1.64 g, 5.0 mmol) was added di-*n*-octyltin(IV) dichloride (2.10 g, 5.0 mmol). The mixture was refluxed for 3 h, the precipitated ammonium chloride removed by filtration, and excess solvent removed under reduced pressure, yielding a pale oil (2.31 g, 62%).

(Tetramethylenedithiocarbamato)triphenyltin(IV), $(C_6H_5)_3SnS_2CN(CH_2)_4$. To a methanol solution (150mL) of ammonium tetramethylenedithiocarbamate (1.48 g, 9.0 mmol) was added triphenyltin(IV) chloride (3.47 g, 9.0 mmol). The mixture was refluxed for 3 h, the precipitated ammonium chloride removed by filtration, and excess solvent removed under reduced pressure, yielding a white powder (3.82 g, 77%).

(Tetramethylenedithiocarbamato)triphenyllead(IV), $(C_6H_5)_3PbS_2CN(CH_2)_4$. To a methanol solution (150 mL) of ammonium tetramethylenedithiocarbamate (0.50 g, 3.0 mmol) was added triphenyllead(IV) chloride (1.42g, 3.0 mmol). The mixture was refluxed for 3 h, the precipitated ammonium chloride removed by filtration, and excess solvent removed under reduced pressure, yielding colorless crystals (1.47 g, 77%).

Crystals of $(C_6H_5)_3SnS_2CNC_4H_8$ (I) and $(C_6H_5)_3PbS_2CNC_4H_8$ (II) were sealed in capillaries and mounted on a Syntex P3 automated diffractometer. Unit-cell dimensions were determined by least-squares refinement of the best angular positions for 15 independent reflections ($2\theta > 15°$) during normal alignment procedures using molybdenum radiation (λ = 0.710 69 Å). Data points (4654 (I) and 4853 (II)) were collected at ambient temperature using a variable scan rate, a θ–2θ scan mode, and a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to a maximum 2θ value of 116°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections, and the intensities of these reflections showing less than 8% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization, and background effects. After removal of space group forbidden data, 2669 (I) and 1720 (II) reflections were considered observed [$I > 3.0\sigma(I)$]. The $(C_6H_5)_3SnS_2CNC_4H_8$ (I) and $(C_6H_5)_3PbS_2CNC_4H_8$ (II) analogues are isostructural and crystallize in isomorphous unit cells. The atomic coordinates and unit-cell dimensions of II may be transformed to those isomorphous with results for I by the matrix.

$$\begin{matrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{matrix}$$

Both structures were solved[6] in space group *Pcab*, a version of no. 61, *Pbca*. Refinement[7] for II progressed to 8.3% with refinement of positional and anisotropic thermal parameters for the 27 non-hydrogen parameters. Hydrogen positional parameters were calcualted by using appropriate geometry and a C–H distance of 0.97 Å but were constrained. Disorder is evident in the anisotropic thermal parameters associated with atoms of the phenyl rings and in the derived bond angles and distances for these groups. Better refinement was attained for I where refinement of positional and anisotropic thermal parameters for all non-hydrogen atom and positional and isotropic thermal parameters for the 23 hydrogen atoms progressed to 5.3% [function minimized $\sum(|F_o| - |F_c|)^2$] [$R = (\sum||F_o| - |F_c||/\sum|F_o|) \times 100$]. Anomalous dispersion corrections were made for Sn. Scattering factors were taken from Cromer and Mann[8] except for the scattering factor for Pb which was used as it appears in ref 9. Unit weights were used throughout.

Discussion

The di- and triorganoelement tetramethylenedithiocarbamates were synthesized in 50–80% yield from the

---

(6) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. MULTAN78 "A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data", University of York, England, and University of Louvain, Belgium.

(7) Stewart, J. M. The XRAY System, version of 1976, Technical Report TR-446, Computer Science Center, University of Maryland, College Park, MD.

(8) Cromer, D. T.; Mann, J. B. *Acta Crystallogr. Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321.

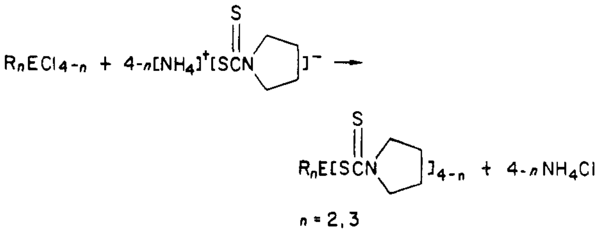
(9) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, 1974; Vol. IV.

Table II. Tin-119m Mössbauer Data (mm s^{-1}) for the Organotin(IV) Tetramethylenedithiocarbamate Derivatives $R_nSn[S_2CN(CH_2)_2]_{4-n}$ (n = 3, 2) at 77 K

compd	IS ± 0.03	QS ± 0.06	Γ_1 ± 0.03	Γ_2 ± 0.03	ρ (= QS/LS)	∠C–Sn–C,[a] deg
$(CH_3)_2SnL_2$[b,c]	1.44	2.84	1.73	1.90	1.97	124
$(C_2H_5)_2SnL_2$	1.65	2.83	0.97	1.01	1.72	123
$(n\text{-}C_4H_9)_2SnL_2$[d]	1.65	2.46	1.06	0.89	1.79	127
$(n\text{-}C_8H_{17})_2SnL_2$	1.58	2.92	1.92	1.96	1.85	125
$(C_6H_5CH_2)_2SnL_2$	1.58	2.45	1.79	1.58	1.55	*e*
$(C_6H_5)_2SnL_2$[e]	1.20	1.70	1.48	1.57	1.42	*g*
$(n\text{-}C_4H_9)_3SnL$	1.44	1.94	1.33	1.30	1.35	
$(C_6H_5)_3SnL$ (I)	1.30	1.90	1.03	1.16	1.46	

[a] Calculated from a point-charge model (see text). [b] L = $S_2CN(CH_2)_4$. [c] Listed as IS = 1.59 and QS = 2.85 mm s^{-1} in ref 10 and 11. [d] Listed as IS = 1.53 and QS = 3.06 mm s^{-1} in ref 10 and 11. [e] No partial QS is available for the benzyl group.[16] [f] Listed as IS = 1.17 and QS = 1.68 mm s^{-1} in ref 10 and 11. [g] The model is not applicable to QS values <2.0 mm s^{-1}.

ammonium salt of the carbamic acid and the organoelement chlorides in refluxing methanol or chloroform (eq 1). The products were oils or solids which were recrys-



(1)

tallized from chloroform. Physical properties, analyses, and yields are gathered into Table I. The dimethyl-, *n*-butyl-, and phenyltin(IV) derivatives were reported[10,11] in 1968 and the trimethyltin(IV) derivative[12] in 1970.

The dithiocarbamate ligand, L, can adopt mono- or bidentate forms, the latter in chelating or bridging configurations of the iso- or anisobidentate type. Ionic forms are also possible but for the title compounds can be ruled out since none are soluble in water. The tendency for chelation and bridging should increase descending the fourth group and maximize at tin(IV) and lead(IV).

A decisive spectroscopic test of association would involve the observation of higher than parent molecular ions in the mass spectrum, but the tin(IV) and lead(IV) derivatives are characterized by loss of organic groups from the metal or loss of L from the diorgano species (see Tables SI–SII).

The infrared and Raman spectra show the ν(C–N) modes in the range 1465–1440 cm^{-1} and the ν(C–S) modes at 1200–1050 cm^{-1} (see Tables SII–SV). However, these data cannot be used to distinguish the bonding modes of the dithiocarbamate ligand.

For the dimethyltin(IV) derivative, the ν(Sn–C) region is clear from interference from ligand bands. In the infrared the absorption at 515 cm^{-1} can be assigned to the asymmetric stretch. This band is absent in the Raman (see Table SV), but a strong band at 478 cm^{-1} can be assigned to the symmetric stretch, a band absent in the infrared. Thus, if these assignments are correct, the compound obeys the selection rules for a linear carbon–tin–carbon skeleton.

The proton NMR data are corroboratory with $|^2J(^{119}Sn\text{–}C\text{–}^1H)|$ = 75.0 Hz and consistent with a six-coordinated geometry at the tin(IV) atom.[13] The $(CH_3)_2Sn$ protons are found at 0.36 ppm, and the two sets of doublets at 1.4 and 2.5 ppm arising from the pyrrolidine ring protons rule out heterocycle configurations frozen with the nitrogen atom out of the ring plane. The rings are either planar or, more likely, in rapid motion.

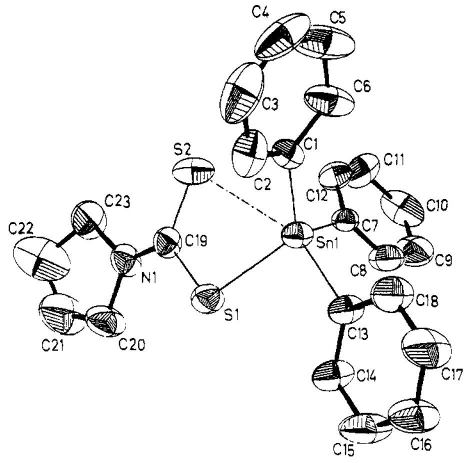


Figure 1. Asymmetric unit of (tetramethylenedithiocarbamato)triphenyltin(IV) (I) showing the atomic numbering.

The tin-119m Mössbauer isomer shift (IS) (see Table II) corroborate tin as tin(IV).[14,15] The quadrupole splittings (QS) produce ρ(= QS/IS) values whose magnitudes are lower than those expected for higher than four-coordinated situations at tin. Only the dimethyltin(IV) derivatives with the highest ρ value would be predicted to be higher than four-coordinated according to the rule which says that values below ~1.8 arise from four-coordinated tin(IV) while those ~2.1 are associated with higher coordination.[14,15]

More particularly, for the diorganotin(IV) derivatives a treatment based upon a point-charge model can be used to relate the QS values to the carbon–tin–carbon bond angle.[16] The results generally correlate well with known structural data[17,18] for dimethyl-[16] and diphenyltin(IV)[19] systems. The calculations, which are based upon the assumption that the contribution of the ligands to the electric-field gradient is negligible, yield the ∠C–Sn–C angles listed in Table II.

For the dithiocarbamates of tin and lead there exists one tin(II) $Sn[S_2CN(C_2H_5)_2]_2$,[20,21] and three lead(II), $Pb(S_2CNR_2)_2$, R = CH_3,[22] C_2H_5,[23,24] and $i\text{-}C_3H_7$,[25] structures

---

(10) Fitzsimmons, B. F. *J. Chem. Soc., Chem. Commun.* **1968**, 1485.

(11) Fitzsimmons, B. F.; Owusu, A. A.; Seeley, N. J.; Smith, A. W. *J. Chem. Soc. A* **1970**, 935.

(12) Dalton, R. F.; Jones, K. *J. Chem. Soc. A* **1970**, 590.

(13) Petrosyan, V. S. *Prog. NMR Spectrosc.* **1971**, *11*, 115.

(14) Zuckerman, J. J. *Adv. Organomet. Chem.* **1970**, *9*, 21.

(15) Zuckerman, J. J. In "Chemical Mössbauer Spectroscopy"; Herber, R. H. Ed.; Plenum Press: New York, 1984; p 267.

(16) Sham, T. K.; Bancroft, G. M. *Inorg. Chem.* **1975**, *14*, 2281.

(17) Zubieta, J. A.; Zuckerman, J. J. *Prog. Inorg. Chem.* **1978**, *24*, 251.

(18) Smith, P. J. *J. Organomet. Chem. Libr.* **1981**, *12*, 97.

(19) Lefferts, J. L.; Molloy, K. C.; Zuckerman, J. J.; Haiduc, I.; Curtui, M. *Inorg. Chem.* **1980**, *19*, 2861.

(20) Potenza, J.; Mastropaolo, D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 1830.

(21) Hoskins, B. F.; Martin, R. L.; Rohde, N. M. *Aust. J. Chem.* **1976**, *29*, 213.

(22) Iwasaki, H. *Acta Crystallogr., Sect B:* **1980**, *B36*, 2138.

Table III. Comparison Structural Data for Dithiocarbamates of Tin and Lead

compound	d(M–S–C=S→M), Å				d(C–N), Å	∠S–M–S, deg	∠S–C–S, deg	ref
	M–S	S–C	C=S	S→M				
tin(II)								
$Sn[S_2CN(C_2H_5)_2]_2$	2.592	1.718	1.682	2.819	1.379	65.9	120.5	20
4 CN,[a] chelated, py[b]	2.765	1.725	1.723	2.574	1.346	67.4	118.8	
	2.57	1.76	1.69	2.78				
	2.58	1.73	1.70	2.83				
lead(II)								
$Pb[S_2CN(CH_3)_2]_2$	2.779	1.736	1.707	2.873	1.32	63.3	119.1	22
4 CN, chelated, py[b]								
$Pb[S_2CN(C_2H_5)_2]_2$	2.786	1.745	1.635	2.940	1.36	61.9	121.4	24
4 CN, chelated, py[b]	2.744	1.724	1.709	2.885	1.38	64.1	121.0	
$Pb[S_2CN(C_3H_7\text{-}i)_2]_2$	2.681	1.729	1.700	2.859	1.33	64.0	117.9	25
4 CN, chelated, py[b]	2.843	1.717	1.714	2.673	1.32	63.9	116.7	
tin(IV)								
$Sn[S_2CN(CH_3)_2]_4$								
$<O_h$, monodentate	2.500	1.74	1.69	3.439	1.30		120.7	26
	2.536	1.71	1.67	3.643	1.40		123.6	
chelated	2.516	1.72	1.69	2.707	1.35		118.5	
	2.510	1.73	1.71	2.595	1.36		118.6	
$Sn[S_2CN(C_2H_5)_2]_4$								
$<O_h$, monodentate	2.502	1.76	1.67		1.34		121	27
chelated	2.529	1.75	1.71	2.554	1.31	70.6	116	
$CH_3Sn[S_2CN(C_2H_5)]_3$	2.481	1.750	1.676	2.817	1.34	67.34	118.9	28
7 CN, chelated	2.619	1.723	1.703	2.772	1.32	65.57	117.1	
	2.618	1.725	1.703	2.749	1.324	66.10	117.4	
$n\text{-}C_4H_9Sn[S_2CN(C_2H_5)_2]_3$	2.619	1.74	1.63	2.820	1.35	65.0	117.0	29
7 CN, chelated	2.741	1.74	1.65	2.674	1.36	65.2	118.5	
	2.491	1.74	1.72	2.763	1.33	68.1	116.9	
$(CH_3)_2Sn[S_2CN(CH_3)_2]_2$	2.515	1.75	1.68	3.061	1.30	63.5	120	30
$<O_h$, chelated	2.497	1.73	1.73	2.954	1.32	65.1	118	
∠C–Sn–C = 136°								
$(CH_3)_2Sn[S_2CN(C_2H_5)_2]_2$								
$<O_h$, chelated								
monoclinic	2.51	1.74	1.66	2.93	1.35	65	120	31
<C–Sn–C = 136.9, 142.8°	2.52	1.74	1.69	3.00	1.33	64	120	
triclinic	2.518	1.747	1.680	2.969	1.330	64.6	119.3	31
∠C–Sn–C = 142.3°	2.536	1.729	1.694	2.918	1.332	65.0	118.8	
orthorhombic	2.488	1.750	1.693	2.938	1.315	63.43	118.4	32
∠C–Sn–C = 135.6°	2.515			3.054	1.473	65.46	119.6	
$(CH_3)_2Sn[S_2CN(CH_2)_4]_2$	2.522	1.75	1.65	2.936	1.38	65.4	121.7	33, 34
$<O_h$, chelated								
∠C–Sn–C = 136°								
$<O_h$, chelated	2.518	1.743	1.685	2.938	1.317	65.43	120.1	35
∠C–Sn–C = 137.3°								
$(C_6H_5)_2Sn[S_2CN(C_2H_5)_2]_2$	2.613	1.72	1.72	2.637	1.31	67.6	116.2	36
$<O_h$, chelated	2.548	1.76	1.72	2.790	1.30	67.6	117.3	
∠C–Sn–C = 101.4°								
$C_6H_5(Cl)Sn[S_2CN(CH_3)_2]_2$	2.528	1.74	1.72	2.661	1.32	69.1	116.8	37
$<O_h$, chelated	2.593	1.75	1.72	2.551	1.32	69.6	116.0	
∠C–Sn–Cl = 94.0°								
$(CH_3)_2ClSnS_2CN(CH_3)_2$	2.79 (ax)	1.74	1.68	2.48 (eq)	1.32	68.2	120	38
5 CN, tbp, eq $(CH_3)_2Sn$								
∠C–Sn–C = 128°								
$n\text{-}C_4H_9(C_6H_5)ClSnS_2CN(CH_3)_2$	2.454	1.742	1.703	2.764	1.319	68.85	118.2	39
4 CN, T_d								
$(CH_3)_3SnS_2CN(CH_3)_2$								
4 CN, $<T_d$								
orthorhombic	2.47	1.80	1.70	3.16	1.35	63	117	41
	2.47	1.78	1.71	3.33	1.34	60	119	
monoclinic	2.47	1.75	1.72	3.16	1.31	62	117	42
$(C_6H_5)_3SnS_2CN(C_2H_5)_2$	2.499	1.76	1.68	3.118	1.32	62.8	118.8	43
4 CN, $<T_d$								
$n\text{-}C_4H_9(C_6H_5)_2SnS_2CN(CH_3)_2$	2.466	1.762	1.680	3.079	1.326	63.81	119.7	40
4 CN, $<T_d$								
$(C_6H_5)_3SnS_2CN(CH_2)_4$								
4 CN, $<T_d$	2.468 (3)	1.776 (11)	1.702 (11)	3.106 (3)	2.267 (14)	63.6 (1)	118.3 (6)	*c*
lead(IV)								
$(C_6H_5)_3PbS_2CN(CH_2)_4$	2.56 (1)	1.82 (3)	1.67 (3)	3.26 (1)	1.25 (5)	60.8 (3)	119 (2)	*c*

[a] CN = coordination. [b] Pyramidal. [c] This work.

plus a dozen tin(IV) structures: $Sn(S_2CNR_2)_4$, R = CH_3[26] and C_2H_5;[27] $RSn[S_2CN(C_2H_5)_2]_3$, R = CH_3[28] and n-C_4H_9;[29] $R_2Sn(S_2CNR'_2)_2$, R = CH_3, R′ = CH_3,[30] C_2H_5 (monoclinic,[31] triclinic,[31] and orthorhombic[32]), and $(CH_2)_4$ (1-

---

(23) Zhdanov, G. S.; Zvonkova, Z. V.; Rannev, N. V. *Sov. Phys.-Crystallogr. (Engl. Transl.)* **1956**, *1*, 407.

(24) Iwasaki, H.; Hagihara, H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *28*, 507.

Table IV. Tin-119m Mössbauer QS Values and C–Sn–C Angles (deg) in $R_2Sn[S_2CNR_2]_2$ Derivatives

compd	QS, mm s^{-1}	ref	∠C–Sn–C calcd[a]	∠C–Sn–C found	ref
$(CH_3)_2Sn[S_2CNR_2]_2$					
R = CH_3	3.04	38	129	136	30
R = C_2H_5	3.14	10, 11	132	136.9, 142.8[b,c]	31
				142.3[d]	31
				135.6[e]	32
R = $(CH_2)_4$	2.84	*f*	123	130	33, 34
	2.85	10, 11	124		
R = C_6H_5	3.20	10, 11	133		
$(CH_3)_2ClSnS_2CN(CH_3)_2$	2.80	38	122	128	38
$(C_6H_5)_2Sn[S_2CNR_2]_2$					
R = CH_3	1.74	38	*g*		
R = C_2H_5	1.76	10, 11	*g*	101.4	36
R = $(CH_2)_4$	1.70	*f*	*g*		
	1.68	10, 11	*g*		

[a] From a point-charge model (see text). [b] Monoclinic form. [c] Two independent molecules. [d] Triclinic form. [e] Orthorhombic form. [f] This work. [g] The model is not applicable to QS values <2.0 mm s^{-1}.

Table V. Crystal Data for (Tetramethylenedithiocarbamato)tin(IV) and -lead(IV), $(C_6H_5)_3SnS_2CNC_4H_8$ (I) and $(C_6H_5)_3PbS_2CNC_4H_8$ (II)[a]

	I	II
formula	$C_{23}H_{23}NS_2Sn$	$C_{23}H_{23}NPbS_2$
M_r, daltons	496.2	584.7
a, Å	23.784 (12)	11.360 (3)
b, Å	16.408 (5)	23.593 (10)
c, Å	11.346 (4)	16.558 (4)
α, deg	90.0	90.0
β, deg	90.0	90.0
γ, deg	90.0	90.0
V, Å^3	4427.8 (30)	4437.9 (25)
F(000)	2000	2256
μ(Mo Kα), cm^{-1}	14.40	89.94
λ(Mo Kα), Å	0.71069	0.71069
ρ_{calcd}, g cm^{-3}	1.488	1.750
Z	8	8
obsd reflctns	2669	1720
R, %	5.3	8.3
space group	*Pcab*	*Pcab*

[a] Estimated standard deviations in parentheses.

pyrrolidine),[33-35] and R = C_6H_5, R′ = C_2H_5;[36] $C_6H_5(Cl)Sn[S_2CN(C_2H_5)_2]_2$,[37] $(CH_3)_2ClSnS_2CN(CH_3)_2$,[38] n-$C_4H_9(C_6H_5)ClSnS_2CN(CH_3)_2$;[39] n-$C_4H_9(C_6H_5)_2SnS_2CN(CH_3)_2$;[40] $R_3SnS_2CNR'_2$, R = CH_3, R′ = CH_3,[41,42] and R = C_6H_5, R′ = C_2H_5.[43] There is as yet no standard against which to differentiate a monodentate S_2CNR_2 attached to lead(II) or lead(IV) from a bidentate group to lead(IV), but the data gathered in Table III can be used to test the validity of the ∠C–Sn–C angles calculated from the QS data in Table II and from literature values. The results are displayed in Table IV. Our results for the title compounds are displayed in Tables V–VIII and SVI–SVIII.

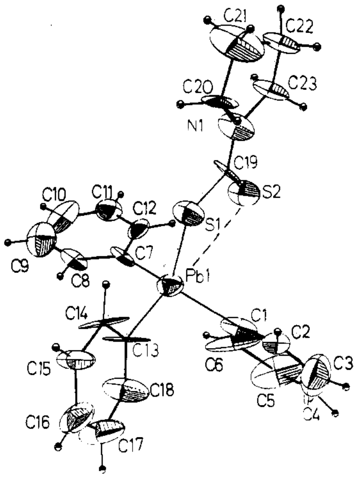


Figure 2. Asymmetric unit of (tetramethylenedithiocarbamato)triphenyllead(IV) (II) showing the atomic numbering.

Table VI. Positional Parameters for (Tetramethylenedithiocarbamato)triphenyltin(IV), $(C_6H_5)_3SnS_2CNC_4H_8$ (I)[a]

atom	*x*	*y*	*z*
Sn1	0.15424 (3)	0.08428 (4)	0.38750 (6)
S1	0.0866 (1)	0.1739 (2)	0.2854 (2)
S2	0.0920 (2)	0.2115 (2)	0.5426 (2)
N1	0.0389 (4)	0.2998 (5)	0.3830 (9)
C1	0.1241 (4)	0.0022 (6)	0.5216 (9)
C2	0.0761 (5)	−0.0347 (7)	0.5131 (12)
C3	0.0576 (6)	−0.0909 (9)	0.6014 (17)
C4	0.0929 (9)	−0.1070 (8)	0.6929 (15)
C5	0.1417 (10)	−0.0736 (9)	0.6990 (12)
C6	0.1631 (7)	−0.0172 (7)	0.6133 (11)
C7	0.2299 (4)	0.1485 (6)	0.4228 (8)
C8	0.2727 (5)	0.1499 (8)	0.3410 (10)
C9	0.3230 (6)	0.1918 (10)	0.3567 (12)
C10	0.3319 (6)	0.2340 (9)	0.4570 (14)
C11	0.2884 (7)	0.2351 (7)	0.5438 (12)
C12	0.2398 (5)	0.1936 (7)	0.5235 (10)
C13	0.1690 (5)	0.0060 (6)	0.2368 (9)
C14	0.1596 (6)	0.0327 (6)	0.1215 (9)
C15	0.1672 (7)	−0.0196 (8)	0.0274 (10)
C16	0.1835 (7)	−0.0988 (7)	0.0458 (11)
C17	0.1902 (8)	−0.1255 (8)	0.1564 (13)
C18	0.1845 (6)	−0.0733 (7)	0.2534 (11)
C19	0.0674 (7)	0.2366 (6)	0.4065 (9)
C20	0.0220 (6)	0.3271 (9)	0.2658 (12)
C21	−0.0088 (9)	0.4049 (11)	0.2893 (18)
C22	−0.0258 (9)	0.4089 (11)	0.4084 (18)
C23	0.0178 (7)	0.3563 (98)	0.4773 (13)
H2	0.022 (8)	−0.012 (13)	0.474 (20)
H3	0.012 (4)	−0.086 (7)	0.591 (10)
H4	0.071 (4)	−0.146 (6)	0.732 (10)
H5	0.182 (5)	−0.089 (8)	0.747 (12)
H6	0.197 (5)	0.004 (7)	0.631 (10)
H8	0.262 (5)	0.102 (7)	0.280 (11)
H9	0.347 (4)	0.190 (5)	0.296 (7)
H10	0.355 (4)	0.267 (5)	0.475 (8)
H11	0.272 (7)	0.274 (10)	0.587 (15)
H12	0.221 (4)	0.201 (5)	0.564 (8)
H14	0.111 (8)	0.061 (12)	0.123 (18)
H15	0.201 (8)	−0.023 (13)	−0.031 (18)
H16	0.172 (8)	−0.158 (11)	−0.018 (17)
H17	0.208 (5)	−0.156 (7)	0.167 (10)
H18	0.198 (5)	−0.094 (7)	0.336 (10)
H201	0.054 (4)	0.323 (6)	0.220 (9)
H202	−0.030 (6)	0.303 (8)	0.248 (13)
H211	0.009 (5)	0.448 (7)	0.292 (10)
H121	−0.025 (5)	0.420 (7)	0.228 (10)
H221	−0.014 (6)	0.468 (8)	0.448 (12)
H222	−0.023 (5)	0.401 (8)	0.423 (12)
H231	0.058 (6)	0.370 (8)	0.517 (11)
H232	−0.020 (6)	0.327 (9)	0.523 (13)

[a] Estimated standard deviations in parentheses.

---

(25) Ito, M.; Iwasaki, H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *36*, 443.

(26) Potenza, J.; Johnson, R. J.; Mastropaolo, D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 941.

(27) Harreld, C. S.; Schlemper, E. O. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1971**, *B27*, 1964.

(28) Morris, J. S.; Schlemper, E. O. *J. Cryst. Mol. Struct.* **1978**, *8*, 295.

(29) Morris, J. S.; Schlemper, E. O. *J. Cryst. Mol. Struct.* **1979**, *9*, 1.

(30) Kimura, T.; Yasuoka, N.; Kasai, N.; Kakudo, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1649.

(31) Morris, J. S.; Schlemper, E. O. *J. Cryst. Mol. Struct.* **1979**, *9*, 13.

(32) Lockhart, T. P.; Manders, W. F.; Schlemper, E. O.; Zuckerman, J. J., submitted for publication.

(33) Lindley, P. F.; Jeffrey, J. W.; Malik, K., quoted in ref 29.

Table VII. Positional Parameters for (Tetramethylenedithiocarbamato)triphenyllead(IV), $(C_6H_5)_3PbS_2CNC_4H_8$ (II)[a]

atom	*x*	*y*	*z*
Pb1	0.3894 (1)	0.1593 (1)	0.0825 (1)
S1	0.2905 (9)	0.0879 (5)	0.1772 (6)
S2	0.5497 (10)	0.0915 (6)	0.2142 (7)
N1	0.388 (3)	0.040 (1)	0.300 (2)
C1	0.525 (3)	0.120 (2)	0.003 (2)
C2	0.512 (4)	0.072 (2)	–0.032 (3)
C3	0.589 (7)	0.052 (2)	–0.086 (5)
C4	0.676 (5)	0.084 (3)	–0.110 (3)
C5	0.707 (4)	0.131 (3)	–0.076 (4)
C6	0.621 (4)	0.156 (3)	–0.020 (2)
C7	0.426 (3)	0.233 (2)	0.148 (2)
C8	0.347 (3)	0.276 (2)	0.154 (2)
C9	0.365 (4)	0.327 (2)	0.200 (4)
C10	0.468 (4)	0.331 (2)	0.239 (3)
C11	0.552 (4)	0.289 (2)	0.240 (3)
C12	0.529 (3)	0.241 (2)	0.195 (2)
C13	0.230 (4)	0.174 (3)	0.004 (2)
C14	0.123 (3)	0.161 (3)	0.031 (2)
C15	0.018 (4)	0.168 (3)	–0.020 (3)
C16	0.042 (4)	0.186 (3)	–0.100 (3)
C17	0.151 (5)	0.197 (3)	–0.128 (2)
C18	0.252 (4)	0.193 (2)	–0.071 (3)
C19	0.416 (3)	0.169 (1)	0.240 (2)
C20	0.278 (4)	0.021 (2)	0.328 (3)
C21	0.292 (5)	–0.010 (3)	0.403 (4)
C22	0.410 (6)	–0.022 (3)	0.407 (4)
C23	0.479 (4)	0.016 (2)	0.354 (3)
H2	0.4443	0.0469	–0.0169
H3	0.5800	0.0125	–0.1144
H4	0.7278	0.0710	–0.1565
H5	0.7821	0.1522	–0.0871
H6	0.6228	0.1979	0.0002
H8	0.2716	0.2711	0.1245
H9	0.3039	0.3580	0.2025
H10	0.4849	0.3661	0.2700
H11	0.6259	0.2937	0.2716
H12	0.5850	0.2090	0.1957
H14	0.1118	0.1472	0.0857
H15	0.0578	0.1595	0.0014
H16	–0.0259	0.1890	–0.1383
H17	0.1640	0.2095	–0.1843
H18	0.3298	0.2045	–0.0882
H201	0.2211	0.0532	0.3321
H202	0.2411	–0.0054	0.2875
H211	0.2693	0.0190	0.4475
H212	0.2359	–0.0397	0.4073
H221	0.4427	–0.0230	0.4613
H222	0.4221	–0.0628	0.3856
H231	0.5203	0.0454	0.3862
H232	0.5429	–0.0037	0.3229

[a] Estimated standard deviations in parentheses.

Table VIII. Bond Angles (deg) and Distances (Å) for (Tetramethylenethiocarbamato)triphenyltin(IV) and -lead(IV), $(C_6H_5)_3SnS_2CNC_4H_8$ (I) *and* $(C_6H_5)_3S_2CNC_4H_8$ (II)[a]

	I, M = Sn	II, M = Pb
	Bond Distances	
M–S1	2.468 (3)	2.56 (1)
M–S2	3.106 (3)	3.26 (1)
M–C1	2.155 (10)	2.23 (4)
M–C7	2.124 (10)	2.09 (4)
M–C13	2.167 (10)	2.25 (4)
C19–S1	1.776 (11)	1.82 (3)
C19–S2	1.702 (11)	1.67 (3)
C19–N1	1.267 (14)	1.25 (5)
N1–C20	1.460 (17)	1.40 (6)
N1–C23	1.502 (17)	1.47 (6)
C20–C21	1.496 (24)	1.46 (9)
C21–C22	1.412 (28)	1.38 (9)
C22–C23	1.558 (25)	1.48 (8)
C1–C2	1.294 (16)	1.26 (3)
C2–C3	1.432 (22)	1.34 (9)
C3–C4	1.361 (26)	1.30 (9)
C4–C5	1.287 (30)	1.30 (10)
C5–C6	1.435 (20)	1.46 (8)
C6–C1	1.431 (17)	1.44 (7)
C7–C8	1.378 (16)	1.35 (5)
C8–C9	1.390 (19)	1.44 (7)
C9–C10	1.349 (21)	1.34 (7)
C10–C11	1.428 (22)	1.38 (7)
C11–C12	1.361 (19)	1.39 (7)
C12–C7	1.381 (14)	1.40 (5)
C13–C14	1.397 (15)	1.33 (6)
C14–C15	1.382 (16)	1.46 (6)
C15–C16	1.372 (18)	1.43 (7)
C16–C17	1.338 (19)	1.34 (7)
C17–C18	1.401 (19)	1.46 (6)
C18–C13	1.367 (16)	1.34 (6)
	Bond Angles	
S1–M–S2	63.6 (1)	60.8 (3)
S1–M–C1	119.1 (3)	113 (1)
S1–M–C7	110.2 (3)	109 (1)
S1–M–C13	95.0 (1)	96 (1)
S2–M–C1	82.0 (3)	80 (1)
S2–M–C7	87.9 (3)	87 (1)
S2–M–C13	157.3 (3)	155 (1)
C1–M–C7	117.3 (4)	121 (1)
C1–M–C13	103.9 (4)	106 (1)
C7–M–C13	107.8 (4)	109 (2)
S1–C19–S2	118.3 (6)	119 (2)
S1–C19–N1	116.7 (8)	114 (2)
S2–C19–N1	124.9 (8)	127 (3)
C19–N1–C20	126.2 (10)	130 (3)
C19–N1–C23	122.3 (10)	121 (3)

[a] Estimated standard deviations in parentheses.

The agreement ranges from 3% for the orthorhombic[32] form of dimethyltin(IV) bis(dithiodiethylcarbamate) to 11% for one of the molecules in the monoclinic[31] form of the same compound. It is not known for which crystal form (or a mixture of the two) the Mössbauer data were recorded.[10,11] All the calculated angles are lower than those found. Inspection of the data leads to the conclusion that the QS values are more affected by change of substituent, R, on nitrogen than is the carbon–tin–carbon angle. In particular, in the monoclinic,[31] triclinic,[31] and orthorhombic[32] forms of dimethyltin(IV) bis(dithiodiethylcarbamate), changes in carbon–tin–carbon angle of 7.2° or 5.3% are seen, while the change from the dimethyl-[30] to the tetramethylenedithiocarbamate[35] results in no change in the dimethyltin(IV) angle. We conclude that, in this series, the calculations from the QS values offer a reasonable guide to the carbon–tin–carbon angles.

Other spectroscopic data yield nonquantitative or less reliable information. While NMR $|^2J(^{119}Sn–C–^1H)|$ values of 84.0[45,46] and 75.0 Hz for the dimethyltin(IV) dimethyl- and tetramethylenedithiocarbamate derivatives, respec-

---

(34) Malik, K. M. A.; Lindley, P. F.; Jeffery, J. W. *J. Bangladesh Acad. Sci.* **1981**, *5*, 53.

(35) Lockhart, T. P.; Manders, W. F.; Schlemper, E. O. *J. Am. Chem. Soc.*, in press.

(36) Lindley, P. F.; Carr, P. *J. Cryst. Mol. Struct.* **1974**, *4*, 173.

(37) Furue, K.; Kimura, T.; Yasuoka, N.; Kasai, N.; Kakudo, M. *Bull. Soc. Chem. Jpn.* **1970**, *43*, 1661.

(38) Harrison, P. G.; Marigia, A. *J. Organomet. Chem.* **1976**, *120*, 211.

(39) Kumar Das, V. G.; Wei, C.; Sinn, E. *Inorg. Chim. Acta*, in press.

(40) Kumar Das, V. G.; Wei, C.; Sinn, E. *J. Organomet. Chem.*, in press.

(41) Sheldrick, G. M.; Sheldrick, W. S. *J. Chem. Soc. A* **1970**, 490.

(42) Sheldrick, G. M.; Sheldrick, W. S.; Dalton, R. F.; Jones, K. *J. Chem. Soc. A* **1970**, 493.

(43) Lindley, P. F.; Aupers, J. H., quoted in ref 29.

(44) deVries, J. L. K. F.; Herber, R. H. *Inorg. Chem.* **1972**, *11*, 2458.

(45) Honda, M.; Komura, M.; Kawasaki, Y.; Tanaka, T.; Okawara, R. *J. Inorg. Nucl. Chem.* **1968**, *30*, 3231.

(46) Otera, J.; Hinoshi, T.; Kawabe, Y.; Okawara, R. *Chem. Lett.* **1981**, 273.

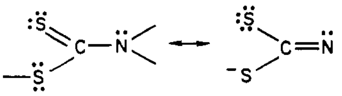
tively, indicate higher than four-coordination in solution,[13] as does the 74.0-Hz value[44] for the dimethylchlorotin(IV) derivative, in agreement with the structures found,[30,33–35,38] the value of 43.0 Hz for methylene chloride and acetone solutions[44] of dimethyltin(IV) bis(dithiodimethylcarbamate) is puzzling in this regard, since it would correspond to a four-coordinate situation.[13] In addition, the infrared and Raman data signal a linear dimethyltin system for the 1-pyrrolidine derivative in which the carbon–tin–carbon angle[35] is 137.3°.

Examination of the structural data gathered in Table III reveals the systematics of the dithiocarbamate ligand in tin and lead chemistry. Both mono- and bidentate chelated ligands are found in the tetrakis tin(IV) derivatives to serve as benchmark data. While no truly isobidentate ligands are found among the 18 compounds studied, one of the chelated rings in diphenyltin(IV) bis(dithiodiethylcarbamate) exhibits identical carbon–sulfur distances and tin–sulfur distances which differ by only 0.024 Å (0.9%).[36] In the other examples it is easy to discern the M—S—C═S system since, with only five exceptions, the shorter carbon–sulfur bond, presumably the *d*(C═S), is associated with the longer sulfur–tin bond, presumably the coordinate-covalent *d*(S→Sn). Likewise, the longer carbon–sulfur bond, *d*(C–S), is associated with the shorter sulfur–tin bond, presumably the ester *d*(S–Sn). The listing in Table VIII is designed to reflect these systematics. Only in bis(dithiodiethylcarbamato)tin(II),[20] bis(dithiodiisopropylcarbamato)lead(II),[25] *n*-butyltin(IV) tris(dithiodiethylcarbamate),[29] phenylchlorotin(IV) bis(dithiodimethylcarbamate),[37] and dimethylchlorotin(IV) dithiodimethylcarbamate[38] are there found chelate rings (one in each) in which the shorter carbon–sulfur bond is not associated with the longer sulfur–tin bond. In the last-named example, the shorter carbon–sulfur bond is associated with the equatorial, and presumably shorter for that reason, sulfur–tin bond, while the longer cation–tin bond is associated with the axial, and presumably longer for the reason, sulfur–tin bond.[38] Otherwise, the generalization is seen to hold quite well, and distinguishing the donor and ester sulfur–tin bonds is a useful first approach to the data.

Excluding the five exceptions named above, the data for the shorter *d*(C–S) fall into the range 1.63–1.73 Å with the longer *d*(C–S), 1.71–1.82 Å.

The lengths of the sulfur–metal linkages should depend upon the metal (Pb > Sn), the oxidation state (II > IV) and the coordination number (CN) (lower CN > higher). In the direct comparison between the bis(dithiodiethylcarbamato)tin(II)[20,21] and -lead(II),[24] the longer *d*(S→M) lie in the ranges 2.77–2.83 Å for the former and 2.89–2.94 Å for the latter, while the shorter *d*(S–M) lie in the ranges 2.57–2.59 Å for the former and 2.74–2.79 Å for the latter. These differences represent a ca. 5% increase in bond length on going from tin(II) to lead(II).

The contiguous carbon–nitrogen bond distances lie in the range 1.25–1.47 Å. A simple valence bond view would correlate these distances inversely with carbon–sulfur bond length through the resonance forms:



Shortening *d*(C–N) would in this model have the further geometric consequence of coplanarity for the four attached groups. It is not known whether piling up charge in the carbon–nitrogen bond would be expected to lengthen both carbon–sulfur bonds to produce a more isobidentate chelate. However, examination of the data, especially at the extremes of the *d*(C–N) range, fails to support the above generalizations.

The sulfur-carbon-sulfur angles in the chelated ligands are found in the range 116–122° with the monodentate ligand angles (range 119.7–123.6°), not very much larger. The interior angles at the metal in the chelates range from 65.9° to 67.4° for tin(II), 61.9° to 64.1° for lead(II), and 60° to 70.6° for tin(IV).

In the tetrakis(dithiocarbamato)tin(IV) derivatives[26,27] two of the ligands are forced into a monodentate configuration to preserve the octahedral, six-coordinated geometry. In the monoorganotin(IV) tris(dithiocarbamates)[28,29] all three ligands participate in chelation even though this means raising the coordination number to seven. All the other derivatives involve chelated ligands until the triorganotin(IV) derivatives are reached. These derivatives show tin distances to the second sulfur atom of 2.94–3.33 Å. The monodentate ligands in tetrakis(dithiodimethylcarbamato)tin(IV) have the second sulfur atom at 3.44–3.64 Å from the tin. However, relatively large distances are also found in the dimethyltin(IV) derivatives[30,33–35] (2.92–3.06 Å) as well. These compounds, for which four structures are available owing to the presence of different crystal forms,[31,32] are best described as adopting distorted octahedral geometries with dimethyltin groups midway between cis and trans. Thus, the line of demarcation between a coordinated and uncoordinated sulfur–tin must lie at ca. 3.1 Å.

In addition, the average *d*(S–Sn) value for the eight determinations of these values in monodentate dithiocarbamates is 2.48 Å (see Table III), while the average of the 48 *d*(S–Sn) and *d*(S→Sn) values for the chelated tin(IV) dithiocarbamates is 2.67 Å.

Against this background it becomes possible to understand the structures of the two title compounds. Taking the tin compound first, the longer tin–sulfur distance is 3.106 (3) Å which is longer than both the shortest nonbonded (3.079 Å in *n*-butyldiphenyltin(IV) dithiodimethylcarbamate[40]) and the longest bonded (3.061 Å in dimethyltin(IV) bis(dithiodimethylcarbamate)[30]) distances as assigned by the authors of previous studies. Thus, the ligand would appear to be monodentate from these data alone. This distance in the presumably isostructural lead analogue is 3.26 (1) Å (0.154 Å or 4.9% longer), but in this series there are no authenticated monodentate dithiocarbamate groups yielding comparison data.

Examination of the angular data yields more decisive conclusions, however. The carbon–tin–carbon and carbon–lead–carbon angles are 109.7° (average) and 112° (average), respectively. The carbon–metal–sulfur angles are 108.1° (average) and 106° (average), respectively, for the tin and lead derivatives. Thus, these molecules are predominantly tetrahedral, and the longer sulfur–metal contacts may be regarded as emanating from monodentate dithiocarbamate ligands. The same conclusion was reached for the orthorhombic[41] and monoclinic[42] forms of trimethyltin(IV) dithiodimethylcarbamate and triphenyltin(IV)[43] dithiodiethylcarbamate.

The average values quoted above mask the large distortions from tetrahedral angles made by the sulfur bond [95.0 (1)–119.1 (3)° for the tin and 96 (1)–113 (1)° for the lead compound] and by the phenyl groups (103.9 (4)–117.3 (4)° for the tin and 106 (1)–121 (1)° for the lead compound). There is no clear-cut progression of angles which would derive from an electronegativity difference between the sulfur and phenyl groups.

The M—S—C═S bonding system is easy to discern in these compounds. The longer *d*(C—S) values (1.776 (11) and 1.82 (3) Å for the tin and lead compounds, respectively) are among the longest recorded (see Table III), and the shorter (d(C—S) values (1.702 (11) and 1.67 (3) Å for the tin and lead compounds, respectively) are among the shortest, as would be expected for a monodentate ligand.

Additional assurance that the four-coordinated geometry is correct comes from the bonded d(Sn–S) value which at 2.468 (3) Å is below the 2.48 Å average of values drawn from the monodentate (dithiocarbamato)tin(IV) determinations and is much smaller than the 2.67 Å average value of the chelated systems. Unfortunately, since ours is the first such determination for a lead(IV) derivative, no comparisons of this kind are possible.

There is no incipient bridging of the ligands in the title compounds. All intermolecular M···S distances are greater than 4.5 Å. The intramolecular S···S distances are 2.986 (3) and 3.009 (15) Å in I and II, respectively. The least-squares planes are listed in Table SVI. The metal–S_2CN systems are quite planar, with the pyrrole rings twisted out of this plane by 8.30–9.96°.

The contiguous d(C–N) values in both title compounds are among the shortest recorded (see Table III). In the valence bond model discussed above, this would be expected to lead to long carbon–sulfur distances and coplanarity for the S_2C and NC_2 systems. The d(C–S) values we record do not seem particularly short, however. Replacing tin(IV) by lead(IV) in the title compound results in an expansion of the metal–sulfur ester bond by 0.09 or 3.7%, and the nonbonded metal–sulfur contact by 0.154 or 5%, but the bonds to the phenyl groups expand by only 0.04 Å or 1.9%.

Acknowledgment. Our work is supported by the Office of Naval Research (J.J.Z.).

Registry No. I, 26879-86-7; II, 97210-85-0; $(C_2H_5)_3GeL$, 97190-96-0; $(CH_3)_2SnL_2$, 26122-22-5; $(C_2H_5)_2SnL_2$, 97190-97-1; $(n\text{-}C_4H_9)_2SnL_2$, 22381-90-4; $(n\text{-}C_8H_{17})_2SnL_2$, 73160-43-7; $(C_6H_5)_2SnL_2$, 22484-01-1; $[NH_4]^+[S_2CN(CH_2)_4]^-$, 5108-96-3; $(C_2H_5)_3GeCl$, 994-28-5; $(CH_3)_2SnCl_2$, 753-73-1; Ph_2SnCl_2, 1135-99-5; $(C_2H_5)_2SnCl_2$, 866-55-7; $(n\text{-}C_4H_9)_2SnCl_2$, 683-18-1; $(n\text{-}C_8H_{17})_2SnCl_2$, 3542-36-7; Ph_3SnCl, 639-58-7; Ph_3PbCl, 1153-06-6.

Supplementary Material Available: Tables of mass spectral data for the R_3ML (Table SI) and R_2ML_2 (Table SII) derivatives, infrared frequencies for the di- (Table SIII) and triorgano (Table SIV) derivatives, Raman frequencies (Table SV), the calculation of planes for I and II (Table SVI), the anisotropic thermal parameters for I (Table SVII) and II (Table SVIII), and structure factors (64 pages). Ordering information is given on any current masthead page.

Synthesis and Reaction of (η^3-1-Methyl-1-(trimethylsilyl)allyl)(μ-dichloro)dipalladium(II). Molecular Structure of *anti*-(η^3-1-Methyl-1-(trimethylsilyl)allyl)chloro(triphenylphosphine)palladium(II)

Toshiyuki Ohta, Takahiro Hosokawa, and Shun-Ichi Murahashi*

Department of Chemistry, Faculty of Engineering Science, Osaka University, Machikaneyama, Toyonaka, Osaka 560, Japan

Kunio Miki and Nobutami Kasai

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565, Japan

Received April 5, 1985

The reaction of trimethylvinylsilane with $PdCl_2$ in DME in the presence of MeOH at room temperature produces *syn*-(η^3-1-methyl-1-(trimethylsilyl)allyl)(μ-dichloro)dipalladium(II) (1). The anti complex 2 was obtained by heating 1 in $CHCl_3$ at 60 °C. Structural elucidation of syn and anti complexes 1 and 2 has been made by the NMR studies, including Overhauser experiments. X-ray crystallography of the *anti*-(η^3-1-methyl-1(trimethylsilyl)allyl)chloro(triphenylphosphine)palladium(II) (4) confirms the anti structure. The mechanism and stereochemical course for the formation of 1 and 2 are described briefly. The reactions of the π-allyl complexes 1 and 2 with sodium malonate give (*E*)-ethyl 5-(trimethylsilyl)-2-carbethoxy-4-hexenoate (**15**) and its *Z* isomer (**16**), respectively. Similarly, the reactions with *N*-methylaniline give [(*E*)-(and (*Z*))-1-methyl-3-(methylphenylamino)-1-propenyl]trimethylsilane (17 and 18) regio- and stereoselectively.

Introduction

Weber et al. reported that the reaction of $(CH_3)_3SiCH{=}CHPh$ with $PdCl_2$ gave 1,4-diphenyl-1,3-butadiene via vinylpalladium(II) intermediate arising from Pd(II)-induced desilylation.[1] Recently, metal-induced desilylations have been documented for the arylation of vinylsilanes with $[ArPd]^+X^-$[2] and the vinylation of alkenes with $[RCH{=}CHSiF_5]K_2$ and Pd(II) salts.[3] Yamamoto et al. have reported that silylated (π-allyl)palladium complexes are prepared by the reaction of $(CH_3)_3SiCH{=}CH_2$

---

(1) Weber, W. P.; Felix, R. A.; Willard, A. K.; Koening, K. E. *Tetrahedron Lett.* **1971**, 4701.

(2) Kikukawa, K.; Ikenaga, K.; Kono, K.; Toritani, K.; Wada, F.; Matsuda, T. *J. Organomet. Chem.* **1984**, *270*, 277; see also; Hallberg, A.; Westerlund, C. *Chem. Lett.* **1982**, 1993.

(3) Yoshida, J.; Tamao, K.; Yamamoto, H.; Kakui, T.; Uchida, T.; Kumada, M. *Organometallics* **1982**, *1*, 542.

0276-7333/85/2304-2080$01.50/0