The traces of methane and other hydrocarbons observed in the gas chromatographic analysis may have resulted from the hydrolysis of the unknown phase since their presence would not be expected if the dicarbide phase was pure.

From the data of Atoji,[8] it is possible to calculate the radii of the lanthanon ions in the dicarbide phases. Some of these radii are given in Table II, along with the metallic radii calculated from the lattice parameters reported by Spedding, *et al.*[1] The radii calculated from the dicarbide lattice parameters compare favorably with the metallic radii of the lanthanons with the exception of ytterbium. This discrepancy may be explained on the basis of the crystal structure of the metal. As Hall, *et al.*,[9] have shown, the metallic radius of ytterbium in its body-centered cubic crystalline modification, which is stable at high pressures, is 1.75 Å. Since the dicarbide is a body-centered type structure, its metallic radius would be expected to agree more closely with this form of the metal rather than with the closest-packed form of ytterbium that exists normally.

TABLE II

RADII OF LANTHANONS IN THE LANTHANON DICARBIDE PHASE (Å.)

	r_{metallic}[a]	C–C	r_{calcd}[c]
Sm	1.802	1.285[b]	1.880
Eu	1.984[d]	1.285[b]	2.038
Gd	1.802	1.285[b]	1.852
Tb	1.782	1.293	1.820
Yb	1.940 (f.c.c.) 1.75 (b.c.c.)[9]	1.287	1.768

[a] Metallic radius calculated from the lattice constants for the metal. [b] Average C–C distance given by Atoji.[8] [c] Metal radius calculated from the lattice constants of the dicarbide. [d] Calculated from data of F. H. Spedding, J. H. Hanak, and A. H. Daane, *AIME Trans.*, **212**, 379 (1958).

Previous attempts at the preparation of europium carbides have probably failed because the europium dicarbide that formed in the reaction either vaporized from the crucible as a dicarbide or disproportionated and left the reaction vessel in the form of gaseous elemental europium. Similarly, europium tetraboride has never been prepared—europium hexaboride is always the product when the europium sesquioxide and boron are mixed in the proper ratio to give the tetraboride. It would seem from this work that EuB_4 might be prepared by using a procedure similar to the one described above since the excess europium would be prevented from escaping. Preliminary experiments indicate that a higher temperature than is obtainable with a stainless steel bomb is necessary for this reaction to proceed.

Acknowledgment.—The authors gratefully acknowledge the support of the U. S. Atomic Energy Commission, and they wish to thank Mr. George Sturgeon for many helpful discussions.

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CONTRIBUTION FROM THE WM. A. NOYES LABORATORY,
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Coordination Compounds of Organotin and Organolead Halides

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Received July 25, 1963

The 1 to 1 addition compounds which are formed between trialkyl tin chloride or trialkyl lead chloride and the Lewis bases tetramethylene sulfoxide, N,N-dimethylacetamide, or N,N-dimethylformamide are reported. Structural evidence supplied by infrared and n.m.r. spectroscopy has been employed to establish the structure of these adducts as trigonal bipyramidal. The lead–hydrogen and tin–hydrogen n.m.r. coupling constants and equilibrium constants for the formation of some of these adducts in carbon tetrachloride solution are reported and discussed.

Introduction

In contrast to a number of addition compounds reported[2,3] for alkyl and aryl tin halides, the only addition compounds which have been reported for organolead halides are the poorly characterized amine "addition compounds" of triphenyllead chloride.[4] Although the addition compounds of the tin halides have been known for a relatively long time, systematic structural studies of the solids have been initiated only recently (see below). There is also a lack of data concerning the nature of the addition compounds in solution.

Our interest in the relative Lewis acidities of organotin and organolead halides has led us to a detailed investigation of the interaction between the Lewis acids, $(CH_3)_3SnCl$, $(C_2H_5)_3SnCl$, $(CH_3)_3PbCl$, and $(C_2H_5)_3PbCl$, and the Lewis bases, tetramethylene sulfoxide, (TMSO), N,N-dimethylacetamide (DMA), and N,N-dimethylformamide (DMF), in inert solvents, such as carbon tetrachloride and benzene. We have found that the interaction between $(CH_3)_3SnCl$ and TMSO, $(C_2H_5)_3SnCl$ and TMSO, and $(C_2H_5)_3PbCl$ and TMSO results in the formation of 1:1 addition compounds,

(1) Abstracted in part from the Ph.D. thesis of N. A. Matwiyoff, University of Illinois, 1963; National Science Foundation Graduate Fellow, 1960–1963.

(2) R. K. Ingham and H. Gilman, *Chem. Rev.*, **60**, 459 (1960).

(3) D. L. Alleston and A. G. Davies, *J. Chem. Soc.*, 2050 (1962).

(4) L. A. Foster, J. J. Gruntfest, and C. A. Fluck, *J. Am. Chem. Soc.*, **61**, 1687 (1939).

the structures of which necessitate a coordination number of five for tin and lead. A reasonable structure for the adducts which is consistent with data from infrared and nuclear magnetic resonance studies is based on a trigonal bipyramidal configuration about the tin or lead atom—the alkyl group and the group IV atom occupying positions in the trigonal plane, the Cl atom and the TMSO molecule occupying the apical positions. The results of the studies also indicate that the DMA and the DMF adducts are similar to those of TMSO.

After the completion of our work, preliminary X-ray results appeared[5] on the 1:1 addition compound between pyridine and trimethyltin chloride. In the solid state, the methyl groups are situated in trigonal positions coplanar with the tin atom and there is an almost linear Cl–Sn–N (pyridine) arrangement perpendicular to the trigonal plane. This structure for the solid adduct has also been proposed on the basis of infrared data.[6] The coordination number five for tin in the derivatives $(CH_3)_3SnBF_4$,[7] $(CH_3)_3SnClO_4$,[8] and $(CH_3)_3SnNO_3$[8] has also been proposed to account for the infrared spectra of the solids. Equilibrium constants are reported for the adducts formed between the acids $(CH_3)_3SnCl$, $(C_2H_5)_3SnCl$, and $(C_2H_5)_3PbCl$ and the donor tetramethylene sulfoxide. The results are not those predicted by the assignment[9] of a much higher electronegativity to lead(IV) than tin(IV).

Experimental

(A) **Preparation and Purification of Chemicals.**—Fisher Spectranalyzed CCl_4, $CHCl_3$, and C_6H_6 were dried over Linde 4-A Molecular Sieves; no water bands were observed in the infrared spectra of the liquids in 1.0-mm. cells.

Eastman White Label N,N-dimethylacetamide (DMA) was dried over barium oxide for 2 days, refluxed at reduced pressure over fresh barium oxide for 2 hr., and fractionally distilled under reduced pressure. The middle fraction was stored over Linde 4-A Molecular Sieves. Eastman White Label N,N-dimethylformamide was purified and stored in the same manner. After purification, no water could be detected in the amides by gas chromatographic analysis (limit of detection, approximately 0.0001 *M* H_2O). The initial concentration of water in the amides varied from 0.1 to 0.3 *M*.

Tetramethylene sulfoxide (TMSO) (Wateree Chemical Co.) was stored over barium oxide for 1 week. It was then refluxed (at reduced pressure) over fresh barium oxide for several hours and fractionally distilled at reduced pressure. The middle fraction was then recycled, and the middle fraction obtained from the recyclization was stored in sealed brown bottles.

Anal. Calcd. for $(C_2H_2)_4SO$: C, 46.12; H, 7.74. Found: C, 46.34; H, 7.82.

The only impurity observed (by gas chromatographic analysis) in the TMSO was water, the concentration of which was less than 0.0001 *M*. In neither the tetramethylene sulfoxide nor the amides could water bands (free and hydrogen-bonded) be observed in the spectra of the liquids in 1.0-mm. cells.

Diethyl ether, Mallinckrodt anhydrous reagent, was distilled from $LiAlH_4$ prior to use.

Trimethyltin chloride was obtained from the Metal and Thermit Co. and was purified by sublimation, m.p. 37.5° (lit.[10] m.p. 37.0°).

Triethyltin chloride was prepared by the treatment of tetraethyltin with stannic chloride[11] and then was fractionated under reduced pressure. The middle fraction was retained, b.p. 103.0° (16 mm.) (lit.[11] b.p. 89–91° (12 mm.)).

Anal. Calcd. for $(C_2H_5)_3SnCl$: C, 29.86; H, 6.27. Found: C, 30.03; H, 6.21.

The tetraethyltin was prepared from $SnCl_4$ by the method of Luijten and van der Kerk.[11] The tin compounds were stored in brown bottles and kept in a vacuum desiccator containing $CaCl_2$.

Trimethyllead chloride was prepared from tetramethyllead by the method of Heap and Saunders[12] and was precipitated several times from benzene solutions by the addition of petroleum ether (boiling range 30–50°).

Anal. Calcd. for $(CH_3)_3PbCl$: C, 12.52; H, 3.15. Found: C, 12.79; H, 3.20.

Triethyllead chloride was prepared from tetraethyllead (obtained from the Ethyl Corp.) by the method of Heap and Saunders.[12] The organolead chlorides treated in this section also appear to be extremely heat and light sensitive. The decomposition reactions ultimately produce lead(II) chloride which, being insoluble in solvents such as benzene and CCl_4, can interfere with the study of the properties of the organolead chlorides. A precursor of lead(II) chloride is probably R_2PbCl_2.

Because triethyllead chloride was to be used in equilibrium constant studies, extra precautions were taken in its purification and storage. Recrystallizations from diethyl ether (dried with $LiAlH_4$) were performed at room temperature in a dark room. The products of recrystallization, after having been freed of excess ether by a stream of dry nitrogen, were stored in brown bottles at Dry Ice–acetone temperatures. Triethyllead chloride purified in the manner described above could be used to prepare *clear* CCl_4 solutions, which were assumed to be free of $(C_2H_5)_2PbCl_2$.

Anal. Calcd. for $(C_2H_5)_3PbCl$: C, 21.85; H, 4.58; Pb, 62.82. Found: C, 22.02; H, 4.78; Pb, 62.71.

(B) **Preparation of Solutions.**—The solutions used in this work were prepared with the aid of pipets and volumetric flasks which had been rinsed with acetone, heated at 100° for several hours, and flushed with dry nitrogen prior to use. The transfer of hygroscopic materials (DMA, DMF, TMSO, and $(C_2H_5)_3SnCl$) was performed in a drybox.

(C) **Nuclear Magnetic Resonance Spectra.**—The Sn^{117}–H, Sn^{119}–H, and Pb^{207}–H coupling constant values were determined from n.m.r. spectra obtained on a Varian Model A-60 high resolution nuclear magnetic resonance spectrometer. The coupling constant values are reproducible to within at least ±1 c.p.s.

(D) **Infrared Spectra.**—Infrared spectra in the region 4000–950 cm.$^{-1}$ were obtained through the use of a Beckman Model IR-7 spectrophotometer. Matched sodium chloride cells, the path lengths of which were 0.2, 0.4, and 1.0 mm., were used.

Infrared spectra in the region 300–900 cm.$^{-1}$ were obtained through the use of a Beckman Model IR-5A spectrophotometer. Cesium bromide cavity cells, the path lengths of which were 0.5 and 1.0 mm., were used to obtain the solution spectra.

(1) **Equilibrium Constants for the Association of TMSO with $(CH_3)_3SnCl$, $(C_2H_5)_3SnCl$, and $(C_2H_5)_3PbCl$.**—When TMSO interacts with tin and lead compounds of the type R_nMCl_{4-n} in CCl_4 solutions, the stretching frequency of the sulfoxy group is lowered. Likewise, the stretching frequency of the carbonyl group in DMA is lowered when DMA interacts with the group IV Lewis acids. In Fig. 1 are reproduced the infrared spectra for the system TMSO–$(CH_3)_3SnCl$. Curve B in Fig. 3 is the absorption spectrum for the free S–O group in TMSO, whereas curve C is the absorption spectrum for coordinated TMSO (the

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[5] R. Hulme, *J. Chem. Soc.*, 1524 (1963); (b) I. R. Beattie, G. P. McQuillan, and R. Hulme, *Chem. Ind.* (London), 1429 (1962).

[6] I. R. Beattie and G. P. McQuillan, *J. Chem. Soc.*, 1519 (1963).

[7] B. J. Hathaway and D. E. Webster, *Proc. Chem. Soc.*, 14 (1963).

[8] R. Okawara, B. J. Hathaway, and D. E. Webster, *ibid.*, 13 (1963).

[9] A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 269 (1958); *ibid.*, **20**, 167 (1961).

[10] C. A. Kraus and C. C. Callis, *J. Am. Chem. Soc.*, **45**, 2628 (1923).

[11] J. G. A. Luijten and G. J. M. van der Kerk, "Investigations in the Field of Organotin Chemistry," Tin Research Institute, Middlesex, England, 1955.

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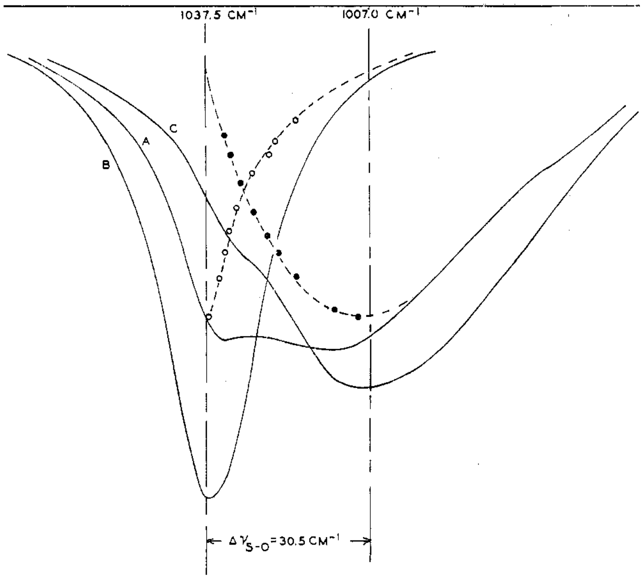

Fig. 1.—Infrared spectra for the system TMSO–$(CH_3)_3SnCl$: A, 0.05 *M* TMSO and 0.25 *M* $(CH_3)_3SnCl$; B, 0.05 *M* TMSO; C, 0.05 *M* TMSO and 0.51 *M* $(CH_3)_3SnCl$; O, resolved absorption curve for free TMSO in solution A; ●, resolved curve for complexed TMSO in this solution.

shoulder near 1037.5 cm.$^{-1}$ is due to a small quantity of free TMSO). The S–O frequency shift, $\Delta\nu_{S-O}$ = 30.5 cm.$^{-1}$, is the difference in the absorption frequencies (at the peak maxima) of the free and coordinated TMSO.

The changes in the absorption intensity for the S–O groups of TMSO in the presence of Lewis acids were used to calculate the equilibrium constants for the formation of the complexes.

The following equation has been derived[13] for the rigorous calculation of equilibrium constants for 1:1 adducts

$$K^{-1} = \frac{A^{T} - A_{0}}{\epsilon_{C} - \epsilon_{D}} - (C_{D} + C_{A}) + \frac{C_{D}C_{A}(\epsilon_{C} - \epsilon_{B})}{A^{T} - A^{0}} \qquad (1)$$

in which C_D and C_A represent the initial concentrations of donor D and acid A, ϵ_C and ϵ_B represent the molar absorptivities of C and D, respectively, A^0 is the absorbance (at a given wave length) which corresponds to that for the initial concentration of D, and A^T represents the absorbance (for the same wave length at which A^0 is determined) of a solution containing A, D, and C.

Equation 1 was solved graphically[13] (Fig. 2) to obtain the equilibrium constants for the association of TMSO with the acids, $(CH_3)_3SnCl$, $(C_2H_5)_3SnCl$, and $(C_2H_5)_3PbCl$. For the determination of *K* for a given system, $A^T - A^0$ values were obtained for four solutions (only three solutions were employed for the $(C_2H_5)_3PbCl$ system) which contained the same concentration of TMSO but different concentrations of the Lewis acid, R_3MCl.

The measurements were obtained at the wave length, 1040 cm.$^{-1}$, on the infrared absorption band of the sulfoxy group in TMSO where the $A^T - A^0$ values are largest. An equilibrium constant was also calculated from the $A^T - A^0$ values at 1050 cm.$^{-1}$ for the system TMSO–$(CH_3)_3SnCl$. The A^T and A^0 values were measured separately using a given set of 0.4-mm. cells, after having established a base line for each *A* value in the conventional manner. The solutions of TMSO, $(C_2H_5)_3PbCl$, $(CH_3)_3SnCl$, and $(C_2H_5)_3SnCl$ were prepared at 25.0 ± 0.1° by the dilution of master solutions (prepared by weighing reagents directly into volumetric flasks followed by dilution with CCl_4). To minimize photochemical decomposition, volumetric flasks wrapped with black tape were used for the preparation of triethyllead chloride solutions. Prior to the measurement of the A^T and A^0 values, the solutions and infrared cells were equilibrated to the temperature 35 ± 1° in the cell chamber. The concentrations of TMSO and the Lewis acids were then corrected for volume changes.

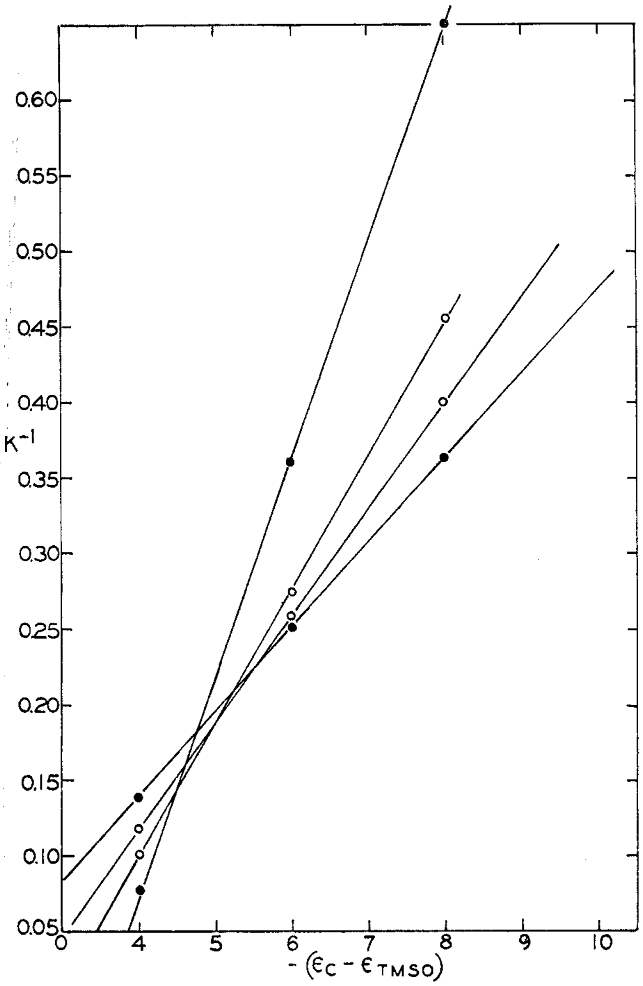

Fig. 2.—Plot of K^{-1} *vs.* $\epsilon_C - \epsilon_B$ for the system TMSO–$(CH_3)_3SnCl$ at 1050 cm.$^{-1}$.

Within the time necessary to obtain the A^T values, no detectable precipitates developed in the solutions of triethyllead chloride, indicating these solutions were free of the slightly soluble diethyllead dichloride. Only after the solutions were kept at 35° for several hours were small amounts of white precipitates detectable.

(2) **Far-Infrared Spectra.**—In order to investigate the effect of the Lewis bases, DMA and TMSO, on the tin–carbon, tin–chlorine, and lead–carbon stretching vibrations in the compounds $(CH_3)_3SnCl$ and $(CH_3)_3PbCl$, infrared spectra in the region 900–286 cm.$^{-1}$ were recorded for solutions in benzene, the compositions of which were varied within the following limits: (a) $(CH_3)_3SnCl$ 0.02–0.04 *M*, TMSO 0.02–1.10 *M*, and DMA 0.02–1.10 *M*; (b) $(CH_3)_3PbCl$ 0.02 *M*, TMSO 0.05–0.35 *M*, and DMA 0.05–0.35 *M*.

Benzene was used for the investigation since it does not absorb strongly in the regions of interest. Since matched cesium bromide cells were not available, the slight overlapping of medium intensity absorption bands from the donors was corrected for by subtracting a base line for each system from the recorded spectrum. The base lines were taken as the absorption spectra of the Lewis bases in benzene at the same concentrations as those used to obtain the spectra for the donor–acceptor systems. The resulting spectra are reproduced in Fig. 3 for the system DMA–$(CH_3)_3SnCl$. Band III is assigned to the Sn–Cl stretching mode, and band II and band I are assigned to the Sn–C symmetric and asymmetric stretching modes, respectively (see Results and Discussion).

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[13] N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, **81**, 6138 (1959).

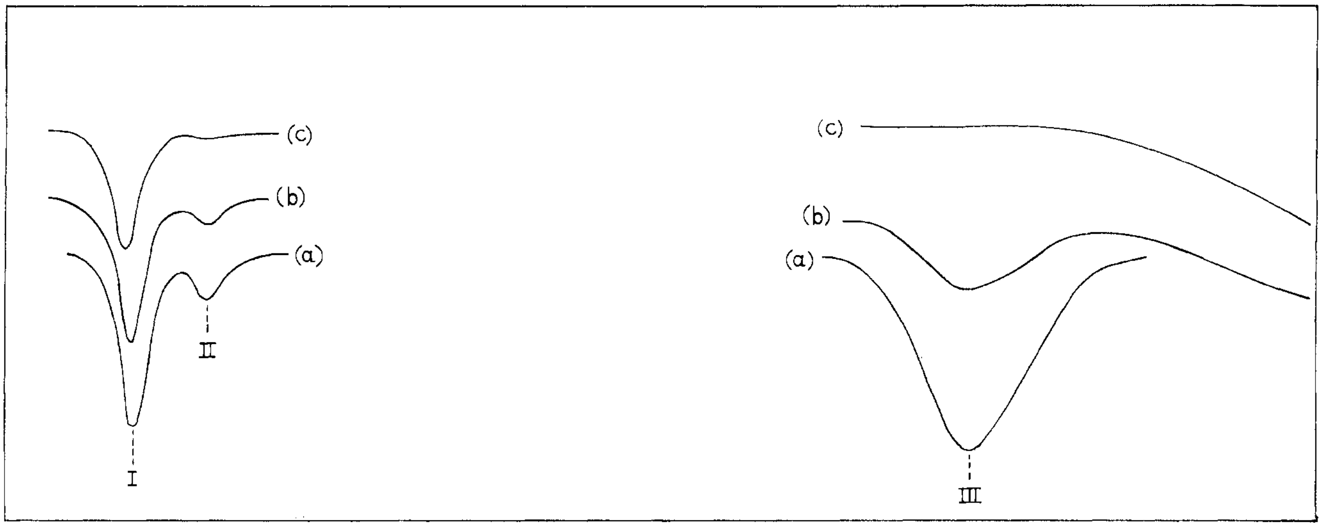

Fig. 3.—Far-infrared spectra for the system DMA–$(CH_3)_3SnCl$: a, 0.024 M $(CH_3)_3SnCl$; b, 0.024 M $(CH_3)_3SnCl$ and 0.1973 M DMA; c, 0.024 M $(CH_3)_3SnCl$ and 1.09 M DMA.

Table I

Equilibrium Constant Determinations[a]

				From crossings		
C_B, M	C_A, M	$A^T - A^0$	Temp., °C.	$-\epsilon_C - \epsilon_B$	K^{-1}	K, l. mole^{-1}
$(CH_3)_3SnCl$–TMSO at 1050 cm.$^{-1}$						
0.0511	0.0509	0.045	35 ± 1	5.45	0.2200	4.55
0.0511	0.1518	0.105	35 ± 1	5.20	0.2075	4.82
0.0511	0.2545	0.140	35 ± 1	5.05	0.1900	5.26
0.0511	0.5102	0.175	35 ± 1	4.75	0.1825	5.48
				4.65	0.1600	6.28
				4.50	0.1425	7.01
$K_{35°} = 5.5 \pm 0.8$ l. mole^{-1}						
$(CH_3)_3SnCl$–TMSO at 1040 cm.$^{-1}$						
0.0511	0.0509	0.111	35 ± 1	10.95	0.1638	6.10
0.0511	0.1518	0.246	35 ± 1	12.15	0.2000	5.00
0.0511	0.2545	0.321	35 ± 1	12.85	0.2400	4.18
0.0511	0.5102	0.436	35 ± 1	11.90	0.1855	5.39
				10.75	0.1600	6.25
				10.65	0.1563	6.40
$K_{35°}{}^{b} = 5.6 \pm 0.6$ l. mole^{-1}						
$(C_2H_5)_3SnCl$–TMSO at 1040 cm.$^{-1}$						
0.0300	0.0500	0.067	35 ± 1	9.5	0.141	7.08
0.0300	0.1000	0.110	35 ± 1	10.75	0.167	5.98
0.0300	0.1500	0.145	35 ± 1	10.90	0.171	5.85
0.0300	0.2000	0.170	35 ± 1	11.25	0.183	5.46
				11.75	0.200	5.00
				12.50	0.220	4.55
$K_{35°} = 5.7 \pm 0.8$ (l. mole^{-1})						
$(C_2H_5)_3PbCl$–TMSO at 1040 cm.$^{-1}$						
0.0200	0.0230	0.038	35 ± 1	21.25	0.2150	4.65
0.0200	0.0520	0.078	35 ± 1	17.90	0.2000	5.00
0.0200	0.0800	0.108	35 ± 1	17.75	0.1700	5.88
$K_{35°} = 5.1 \pm 1.1$ l. mole^{-1}						

[a] See Experimental section for definition of symbols. [b] For the values of K the error was estimated at the 90% confidence level from the equation [H. A. Laitinen, "Chemical Analysis," McGraw-Hill Book Co., New York, N. Y., 1960, pp. 547–548]: $K = X + C_nR$, in which X represents the mean of n values, R represents the difference between the smallest and largest values, and C_n is a constant dependent upon the value of n.

(E) Molecular Weights.—With the exception of the value for trimethyltin chloride, the molecular weights reported here were determined by Mr. J. Nemeth and his staff at the University of Illinois Microanalytical Laboratory by means of a Mechrolab vapor phase osmometer. The value for the molecular weight of trimethyltin chloride was determined by Dr. D. A. Bafus, who used a cryoscopic technique [14]

Results and Discussion

(A) Equilibrium Constant Studies.—Since in the plots of K^{-1} vs. $\epsilon_C - \epsilon_B$ for the TMSO–$(CH_3)_3SnCl$, TMSO–$(C_2H_5)_3SnCl$, and the TMSO–$(C_2H_5)_3PbCl$ systems, the lines which correspond to distinct values of $A^T - A^0$ intersect within small areas, it can be safely concluded that $(CH_3)_3SnCl$, $(C_2H_5)_3SnCl$, and $(C_2H_5)_3PbCl$ all form 1:1 addition compounds with TMSO. In Table I the data for the equilibrium constant determinations are summarized.

The formulation of these equilibria by the general equation

$$R_3MCl + D \rightleftharpoons R_3MCl \cdot D \qquad (2)$$

is supported by molecular weight studies on the Lewis acids. The molecular weight determined for trimethyltin chloride in a 0.05 M carbon tetrachloride solution is 198.6 (the theoretical value, assuming a nonassociated monomer, is 199.26) and that determined for triethyllead chloride in a 0.01 M carbon tetrachloride solution is 324 (theoretical value, 330).

The main source of error in the equilibrium constants can be attributed to the relatively large error (at least 0.002 absorbance unit) in the absorbance values compared to the difference $A^T - A^0$. The calculation of K for the TMSO–$(CH_3)_3SnCl$ system from the $A^T - A^0$ values at 1040 cm.$^{-1}$ results in an error in K of ±0.6, whereas the calculation of K from the smaller values of $A^T - A^0$ at 1050 cm.$^{-1}$ results in an error of ±0.8. The equilibrium constants have been determined for those conditions in which the concentration of the Lewis acid is greater than that of the Lewis base. It is assumed that DMA and DMF, which have

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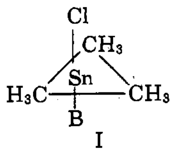
(14) D. A. Bafus, Ph.D. Thesis, University of Illinois, 1963.

similar donor properties to TMSO,[15] will also form 1:1 adducts with the Lewis acids R_3MCl.

The basic site in TMSO and the amides is the oxygen atom of the sulfoxy group and the carbonyl groups, respectively. Large contributions to the ground state of TMSO and the amides from double bonded structures such as $S{=}O$[16,17] and $C{=}O$[18] enhance the force constants for the S–O and C–O bonds. Coordination of the oxygen atom to a Lewis acid decreases the force constants (and stretching frequencies) for the S–O and C–O bonds in TMSO and the amides. This decrease in stretching frequency of the S–O bond in sulfoxides and the C–O bond in amides has been observed for many sulfoxide–Lewis acid[19] and amide–Lewis acid[20] systems and has been interpreted in terms of the coordination of the oxygen atom to the Lewis acid.

The values of the frequency shifts, $\Delta\nu_{SO}$ and $\Delta\nu_{CO}$, for the interaction of TMSO and the amides with the Lewis acids studied here are approximately the same ($\Delta\nu_{SO}$ for each of the acids is 27 ± 3 cm.$^{-1}$ and $\Delta\nu_{CO}$ is 26 ± 3 cm.$^{-1}$). This similarity indicates that there is no differentiation in the abilities of $(CH_3)_3SnCl$, $(C_2H_5)_3SnCl$, $(CH_3)_3PbCl$, and $(C_2H_5)_3PbCl$ to polarize the CO or SO bond. For the acids studied in this work, the relative values of the equilibrium constants and the similarity in the frequency shifts indicate that the relative strengths of the Lewis acids are approximately the same; the large error limits in the equilibrium constants, in conjunction with the small changes in the equilibrium constant with temperature, precluded the determination of accurate enthalpies of reaction by the infrared method).

Since an ionic structure for the 1:1 adducts can be excluded on the basis of our finding that all the R_3MCl species studied in this work[21] are nonconductors in dry TMSO and DMA, the coordination number of five for tin and lead in the adducts is necessary. A number of basic structural types are possible for the coordination number five, the two most reasonable of which are the trigonal bipyramid (I) and the tetragonal pyramid (II). Distortions from the simple structures depicted could arise from the bonding requirements of different groups in supposedly equivalent environments, *e.g.*, in I the distance from the tin atom to the groups B and Cl might not be identical and the angle defined by the groups Cl–Sn–B might not be 180°. There are four geometrical isomers possible for each of the structural types, I and II. The data from the studies of the far-infrared and nuclear magnetic resonance spectra of systems reported here are consistent with the isomer depicted by I.



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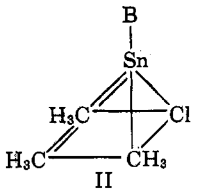

II

(B) **Far-Infrared Spectra.**—The Raman and infrared spectra of trimethylin chloride have been studied intensively.[22,23] The absorption bands at 545 and 514 cm.$^{-1}$ have been assigned to the tin–carbon asymmetric and symmetric stretching vibrations, respectively. The band at 315 cm.$^{-1}$, for the liquid compound, has been assigned to the tin–chlorine stretching mode. In benzene solutions the frequency of the tin–chlorine stretching vibration shifts to 332 cm.$^{-1}$, but the Sn–C symmetric and asymmetric stretching frequencies are unchanged. In Lewis base–trimethyltin chloride systems, marked changes are observed in the far-infrared spectra. As the ratio of the number of moles of the Lewis base to the number of moles of trimethyltin chloride dissolved in benzene is increased, the tin–carbon symmetric stretching vibration disappears, the tin–chlorine stretching frequency is shifted from 332 cm.$^{-1}$ to less than 286 cm.$^{-1}$, and the tin–carbon asymmetric stretching frequency is increased from 545 to 552 cm.$^{-1}$. These changes are consistent only with the formation of an addition compound which has the structure I.

Isomer I has C_{3v} symmetry and, although the tin–carbon symmetric mode is not symmetry forbidden (as it is in D_{3h}), a very weak band is expected because of the low dipole moment change associated with this vibration. The asymmetric stretching frequency is infrared-active. That the asymmetric tin–carbon stretching frequency is higher and the tin–chlorine stretching frequency is lower in the addition compound than in trimethyltin chloride can be rationalized if one assumes that the hybridization of the orbitals which the tin atom employs in bonding the groups in the trigonal plane is very nearly sp^2, whereas that for the axial bonds is nearly pd or pure p. The correlation of the increase in s character for a given bond with the increase in the stretching frequency for the atoms connected by the bond has been observed for many systems.[24,25] It should be pointed out, however, that the status of the hybridization of the orbitals involved in the trigonal and the axial bonds in trigonal bipyramidal molecules is by no means clear.[26,27] The problem of the hybridization of the tin atom, which contains three different substituents, in the isomer depicted for structural type I is more complicated than the systems that have been treated.[26,27] However, in view of the infrared results presented and some n.m.r. results

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TABLE II[a]

COUPLING CONSTANTS, Pb^{207}–H, Sn^{117}–H, AND Sn^{119}–H, FOR THE SYSTEMS LEWIS BASE–$(CH_3)_3MCl$

		Lewis base, *M*			Coupling constant, c.p.s.		
$(CH_3)_3SnCl$, *M*	$(CH_3)_3PbCl$, *M*	TMSO	DMA	DMF	Pb^{207}–H	Sn^{117}–H	Sn^{119}–H
1.449						55.5	58.5
1.449		1.449				64.0	67.0
0.992		4.959				66.0	69.0
1.449		Pure solvent				68.0	70.0
1.449			1.449			63.0	65.5
0.992			4.959			65.0	68.0
1.449			Pure solvent			68.0	70.0
1.449				1.449		62.5	65.5
1.449				Pure solvent		68.0	70.0
	1.5 ($(CH_3)_4Pb$)				62.0		
	Saturated				69.5		
	Saturated		0.20		77.3		
	Saturated		Pure solvent		83.5		
	Saturated			Pure solvent	83.5		

[a] The coupling constants were obtained from the spectra of solutions in benzene except for those rows marked pure solvent, in which case the appropriate Lewis base was used as the solvent. The coupling constants were also obtained from the spectra of solutions of trimethyltin chloride and Lewis bases in carbon tetrachloride solutions, but the coupling constants were identical with those obtained from the spectra of benzene solutions. It was necessary to use benzene as the solvent for the lead compounds since they are only slightly soluble in carbon tetrachloride.

to be discussed shortly we conclude that the tin atom will employ more s character in the bonds in the trigonal plane of the addition compound than it employs in the bonds to the methyl groups in trimethyltin chloride. The polarization of the Sn–Cl bond (in the sense $B \cdots\cdots Sn^{+} \cdots\cdots Cl^{-}$) in the addition compound is accompanied by bond lengthening which can be considered to arise from the incorporation by the tin atom of pure p or of p and d character in the Sn–Cl bond at the expense of s character.

The orbital(s) which tin utilizes in bonding the axial groups could be the hybrid orbital ($p_z + d_z{}^2$) or, in view of the recent discussions[28] of the application of three-center molecular orbitals to describe the bonding between atoms of low electronegativity and Lewis bases or anions (*e.g.*, to describe the bonding in I_3^- and ICl_2^-),[28b] this bonding orbital could be essentially p_z. According to these arguments, the three-center molecular orbitals in the addition compound $(CH_3)_3SnCl{\cdot}B$ would involve the linear combination of the tin p_z-orbital and two orbitals of the proper symmetry, one each from the Cl atom and the oxygen atom of the base molecule to produce the following set of three molecular orbitals: (1) A bonding orbital involving B, Sn, and Cl, but polarized toward Cl, the most "electronegative" center, (2) an essentially nonbonding orbital concentrated on B and Cl, and (3) an antibonding orbital. The four electrons involved in the B–Sn–Cl bond would occupy the two lower energy bonding and nonbonding orbitals. On this basis then, it is reasonable to expect that the Sn–Cl bond should be weaker and the stretching force constant should be smaller in the addition compound. However, it must be pointed out that the absence of a contribution to the bonding from the d-orbital has not been experimentally demonstrated and since the d_z-orbital has appropriate symmetry and does overlap with the axial groups, some contributions to the bonding from this orbital are expected.

The carbon–lead stretching frequency for trimethyllead chloride can be assigned to the band at 492 cm.$^{-1}$, which is the only band that appears below 700 cm.$^{-1}$ in the spectra of benzene solutions or Nujol mulls of trimethyllead chloride. The lead–chlorine stretching frequency is apparently less than 286 cm.$^{-1}$. That only one lead–carbon stretching frequency is discernible can probably be attributed to the accidental degeneracy which is expected for the low frequency fundamentals of molecules having heavy central elements[22] (a 0.01 *M* solution of $(CH_3)_3PbCl$ in benzene exhibits the molecular weight expected for a nonassociated monomer). The behavior of trimethyllead chloride in the presence of Lewis bases is also similar to that of trimethyltin chloride—the carbon–lead stretching frequency is increased from 492 to approximately 497 cm.$^{-1}$. This increase can be rationalized on the basis of the formation of an addition compound, of structural type A.

(C) Tin–Proton and Lead–Proton Coupling Constants.—Holmes and Kaesz [29] have developed a linear correlation between the tin–hydrogen spin–spin coupling constants in methyltin derivatives and the amount of s character that the tin atom presumably employs in bonding the methyl groups. In establishing the linear relationship, it was assumed that the Fermi contact interaction[30] makes the dominant contribution to the Sn–H coupling constant and that, except for the rehybridization of the tin atom, other components of the bonding system Sn–C–H do not change appreciably. Taking as one point the observed coupling constant for tetramethyltin, which was considered to represent 25% s character, and the origin as the second point,

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[30] Recently Klose (G. Klose, *Arch. Sci. Geneva*, **14**, 427 (1961)) has reported that from a valence bond treatment of methyltin and ethyltin systems, it can be concluded that the Fermi contact interaction term makes the dominant contribution to the spin–spin coupling interaction between the tin atom and the proton.

Holmes and Kaesz generated a straight line. Aside from the theoretical uncertainties concerning a linear relationship, it does not seem unreasonable to conclude that the Sn–H coupling constants in methyltin derivatives will increase with an increase in the amount of s character in the Sn–C bond.

In Table II, the coupling constants are collected for the systems Lewis base–$(CH_3)_3MCl$, in which M represents tin and lead. In the table, data for tetramethyllead are also included.

The coupling constant data, like the far-infrared data, are consistent with the formation of an addition compound which has structure I. The coupling constant values for the Lewis acids dissolved in the Lewis bases can be taken as those for the addition compounds, $B\cdot(CH_3)_3MCl$. The values indicate an appreciable increase in the s character in the M–C orbitals of the M atom in the addition compound with respect to that of the uncoordinated Lewis acids. It is interesting that the value of the Sn–H coupling constant for the system $(CH_3)_3SnCl\cdot B$ requires (from the plot of Holmes and Kaesz[29]) 33% s character in the tin orbitals which are used for bonding the methyl groups. This distribution of s character can readily be rationalized on the basis of structure I where the methyl groups are bonded by essentially sp^2 hybrids. This result does not appear to be consistent with the other possible structures.

Trimethyltin chloride probably is extensively dissociated to the solvated cation in aqueous solutions. For the unsolvated cation $(CH_3)_3Sn^+$ a planar structure based on the utilization of sp^2 hybridization by the tin atom would be expected. From the line generated by Holmes and Kaesz, the experimental Sn–H coupling constant indicates that the tin atom employs 32% s character in Sn–C bonds. It is likely that the addition compound between water and the trimethyltin cation would possess a structure similar to the isomer depicted in I with two water molecules occupying the axial sites. If any un-ionized trimethyltin chloride exists in the aqueous solutions, it may be hydrated and possess a structure similar to I. In the event that un-ionized trimethyltin chloride does exist in aqueous solutions, the Sn–H coupling constant will be a statistical average of those for the distinct solvated species $(CH_3)_3SnCl\cdot H_2O$ and $(CH_3)_3Sn(H_2O)_2^+$ because of the rapid exchange of Cl^- and H_2O which occurs in the aqueous solutions (only one methyl–proton signal is observable at 31°).

If a plot of the amount of s character in the Pb–C orbitals of methyllead compounds *vs.* the Pb–H coupling constants is constructed in a manner similar to that for the methyltin compounds (by taking as one point the origin and as the other point the coupling constant for tetramethyllead, 62.0 c.p.s., which is assumed to represent 25% s character), obviously a straight line can be generated. From this line for the methyllead compounds, the Pb–H coupling constant for the adduct suggests that 33% s character is incorporated by the lead atom in bonding the methyl groups. For the Lewis base–$(CH_3)_3PbCl$ systems, both the far-infrared spectra and the coupling constant data are then consistent with structure I.

Acknowledgment.—The authors wish to acknowledge the generous support of this research by the Titanium Division of The National Lead Corporation.

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Reduction Potentials of Some Chromium(III) Complexes[1]

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Received August 8, 1963

Polarographic reduction of 1:1 Cr(III) complexes of Y^{-4} (EDTA), F^-, $P_2O_7^{-4}$, PO_4^{-3}, and SCN^- in 0.1 *M* $NaClO_4$ gave two reduction waves for each complex. $E_{1/2}$ of the first wave (Cr(III) → Cr(II)) did not vary when excess ligand was subsitituted for $NaClO_4$. For certain systems stepwise variation of $E_{1/2}$ with pH was observed. This variation is interpreted in terms of protonation of the complexes. The shape of the waves indicated reversible reduction of SCN^- and Y^{-4} complexes and less reversible reduction for other species. Half-wave potentials (−v. *vs.* s.c.e.) characteristic of each species at 25° (water omitted) and the corresponding log slopes (θ) are: Cr^{+3}, 0.810 (1.1); CrF^{+2}, 1.060 (1.4); $CrSCN^{+2}$, 0.880 (1.04); $CrP_2O_7H_{n+1}{}^{n+1}$, 1.16 (1.2); $CrP_2O_7H_{n+1}{}^{n}$, 1.27 (1.2); $CrP_2O_7H_n{}^{1-n}$, 1.42 (1.3); $CrPO_4H_{n+1}{}^{n+1}$, 0.80 (1.5); $CrPO_4H_n{}^{n}$, 1.145 (2.7); CrY^-, 1.250 (1.04); HCrY, 0.905 (1.4). At pH 3.0, $E_{1/2}$ becomes more positive in the order: $P_2O_7^{-4}$, Y^{-4}, F^-, PO_4^{-3}, SCN^-. This variation is discussed in terms of the rate of Cr(II) catalyzed formation of the Cr(III) complexes.

Chromium(II) has been shown[2] to be a catalyst for the formation of Cr(III) complexes, the rate of the reaction

$$\mathrm{Cr(III)} + \mathrm{L} + \mathrm{Cr(II)} \leftrightarrows \mathrm{Cr(III)L} + \mathrm{Cr(II)}$$

depending on the nature of the ligand. The reaction is analogous to certain Co(III)–Cr(II) reactions[3] and is considered to involve an OH^- (or H_2O) bridging group which links two Cr atoms during an electron

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[1] Taken from a portion of a Ph.D. thesis submitted (1963) to the Graduate School of Georgetown University by Br. Joseph H. Walsh, S.M., presented in part at the 141st National Meeting of the American Chemical Society, Washington, D. C., April, 1962.

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