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Complexes of 1,8-Naphthyridines. II. Dialkyltin Dichloride Adducts of 2,7-Dimethyl-1,8-naphthyridine[1]

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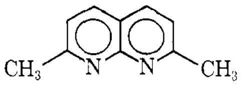
Received March 5, 1969

Complexes of the type R_2SnCl_2I, where R = CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, C_6H_5, $C_{12}H_{25}$ and Cl and I = 2,7-dimethyl-1,8-naphthyridine, have been prepared and characterized. A four-member chelate ring system is exhibited in these white, air-stable complexes. The infrared spectra (600–200 cm^{-1}) of the compounds have been recorded and assignment of the Sn–Cl and Sn–C stretching modes made. The changes in ligand and alkyltin proton magnetic resonance positions produced by complexation are examined. The ^{117}Sn–H and ^{119}Sn–H coupling constants for the compounds where R = CH_3 and C_2H_5 are reported. A *cis*-Cl,*trans*-R geometry for these complexes is inferred from the spectral data.

Introduction

Several stable octahedral addition complexes of dialkyltin dichlorides with nitrogen heterocycles such as pyridine,[1,2] 4-picoline,[3,4] 2,2′-bipyridine,[5,6] and 1,10-phenanthroline[5,6] have been prepared and characterized. The stereochemistry of these and analogous complexes containing oxygen donor ligands[7,8] as inferred from proton magnetic resonance (pmr) and infrared spectra has been the subject of extended discussion.

The isolation of numerous stable octahedral metal complexes of the nitrogen heterocycle 2,7-dimethyl-1,8-naphthyridine[1b,9] (I), wherein the ligand forms a four-member chelate ring, prompted an extension of our studies to include metal centers which are bonded to alkyl groups. Chelation of dialkyltin dichlorides with I does not provide an opportunity to derive stabilization *via* π bonding which is possible in the previously investigated metal carbonyl complexes.[9] Hence, these studies offer an opportunity to compare four- and five-member chelate nitrogen heterocyclic ring systems of similar basicity where π interaction with the metal center is unlikely.



I

Experimental Section

Materials.—Dialkyltin dichlorides purchased from M and T Chemicals Inc., Rahway, N. J., were sublimed or recrystallized prior to use. Fisher tin tetrachloride was used as received. The procedure of Paudler and Kress was used for the preparation of 2,7-dimethyl-1,8-naphthyridine.[10] Reaction solvents of ACS grade were dried over sodium prior to use.

Preparation of R_2SnCl_2I.—All complexes were prepared by the general procedure of mixing 5-ml benzene solutions containing 0.5 mmol of the appropriate organotin dichloride and 0.08 g (0.5 mol) of 2,7-dimethyl-1,8-naphthyridine. After cooling in an ice bath, the white, crystalline, air-stable products were filtered, washed with cold benzene, and dried under vacuum. Complexes containing large alkyl groups required concentration by evaporation before precipitation would occur. Recrystallization from a cyclohexane–benzene mixture yielded the desired complex as confirmed by elemental analysis. The $SnCl_4$ adduct was prepared in a helium atmosphere. Carbon, hydrogen, and nitrogen analyses were determined by combustion.

Anal. Calcd for $SnCl_4(C_{10}H_{10}N_2)$: C, 28.7; H, 2.39; N, 6.68. Found: C, 29.0; H, 2.34; N, 6.83. Calcd for $(CH_3)_2SnCl_2(C_{10}H_{10}N_2)$: C, 38.2; H, 4.25; N, 7.44. Found: C, 38.4; H, 4.42; N, 7.56. Calcd for $(C_2H_5)_2SnCl_2(C_{10}H_{10}N_2)$: C, 41.5; H, 4.93; N, 6.90. Found: C, 41.3; H, 4.95; N, 7.17. Calcd for $(C_3H_7)_2SnCl_2(C_{10}H_{10}N_2)$: C, 44.3; H, 5.54; N, 6.46. Found: C, 44.6; H, 5.55; N, 6.53. Calcd for $(C_4H_9)_2SnCl_2(C_{10}H_{10}N_2)$: C, 46.9; H, 6.06; N, 6.06. Found: C, 47.1; H, 6.16; N, 6.31. Calcd for $(C_5H_{11})_2SnCl_2(C_{10}H_{10}N_2)$: C, 49.1; H, 6.54; N, 5.72. Found: C, 49.4; H, 6.51; N, 5.90. Calcd for $(C_6H_5)_2SnCl_2(C_{10}H_{10}N_2)$: C, 52.6; H, 4.38; N, 5.58. Found: C, 52.8; H, 4.24; N, 5.50. Calcd for $(C_{12}H_{25})_2SnCl_2(C_{10}H_{10}N_2)$: C, 59.5; H, 8.75; N, 4.08. Found: C, 59.9; H, 8.99; N, 4.20.

Spectral Measurements.—Pmr spectra were obtained with a Varian A-60 spectrometer at ambient temperature on deuteriochloroform solutions of the complex containing tetramethylsilane as the internal standard. The ^{119}Sn–H and ^{117}Sn–H coupling constants were measured using a Varian HA-100 spectrometer. A Perkin-Elmer Model 621 spectrometer was used to record the infrared spectra (4000–200 cm^{-1}) of the complexes which were mulled with Nujol. Polystyrene was used to calibrate the spectra. Molecular weight determinations were made on approximately 10^{-3} *M* chloroform solutions using a Mechrolab Model 301A vapor-pressure osmometer.

Results and Discussion

Infrared Measurements.—Numerous studies of infrared spectra of complexed dialkyltin dichlorides are found in the literature.[11-13] Particular interest centers about the Sn–C (500–600 cm^{-1}) and the Sn–Cl (200–300 cm^{-1}) stretching regions. The bands observed in

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(1) (a) Presented at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 10, 1968, No. INOR 69; (b) D. G. Hendricker and T. E. Reed, *Inorg. Chem.*, **8**, 685 (1969), should be considered as part I of this series.

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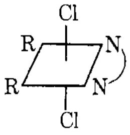
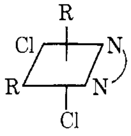
the spectra of the R_2SnCl_2I complexes which are assigned to these modes are given in the text.

In addition to these absorbances, all complexes exhibited bands typical of I coordinated to a metal center.[9] In the region 600–200 cm^{-1} these modes appear at approximately 270, 360, 450, 480, 540, and 580 cm^{-1}. The first three bands have moved to higher energy from the uncomplexed absorptions at 240, 343, and 440 cm^{-1} due to the effect of the metal on ring deformation and ring–CH_3 bending modes.

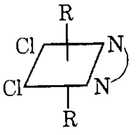
The three possible geometric arrangements for compounds of the type R_2SnCl_2I presuming I must coordinate in a *cis* manner are



cis-R



asym-R



trans-R

The *asym*-R form may be excluded from pmr evidence which will be discussed later. One would expect to observe in the infrared two ν(Sn–Cl) and one ν(Sn–C) for the *trans*-R form and one ν(Sn–Cl) and two ν(Sn–C) for the *cis*-R form.

Complexes of the type R_2SnCl_2(phen) and R_2SnCl_2(bipy) exhibit a strong, broad band at 245 cm^{-1} assigned to ν(Sn–Cl). This absorption sometimes shows a shoulder or separate band at 220 cm^{-1} which has led to the conclusion that these complexes have a *cis*-Cl arrangement.[11–13] Variation of the R group from CH_3 to C_4H_9 causes little change in the position of the Sn–Cl absorbances.

The assignment of ν(Sn–Cl) in the complexes R_2SnCl_2I is complicated by the presence of a ligand absorption at 270 cm^{-1}. When R = CH_3, C_2H_5, and C_4H_9 a strong band at 267 ± 5 cm^{-1} possessing a half-height width of 50 cm^{-1} or greater is observed. This suggests the presence of two or more absorptions and is assigned to include ν_{asym}(Sn–Cl). A distinct second band observed when R = CH_3 and C_3H_7 at 220 and 239 cm^{-1}, respectively, is assigned as ν_{sym}(Sn–Cl) and supports a *cis*-Cl geometry for these complexes.

The spectra of $(C_6H_5)_2SnCl_2I$ exhibits a broad, strong band at 276 cm^{-1}, a sharp, medium band at 235 cm^{-1}, and a band starting to appear at 205 cm^{-1} whose maximum exceeds the limit of the spectrometer. The last two bands assigned to ν(Sn–Cl) modes are similar in position to those reported for the complex $(C_6H_5)_2SnCl_2(DMSO)_2$.[7] The 276-cm^{-1} frequency is typical for a C_6H_5–Sn stretching mode.[14]

It has been pointed out by Tanaka[7] that a *trans*-Cl arrangement exhibits a ν(Sn–Cl) at 345 cm^{-1} while ν(Sn–Cl) for a *cis* arrangement is found in the 245-cm^{-1} region. Thus the position and number of ν(Sn–Cl) modes observed for R_2SnCl_2I complexes suggest a *cis*-Cl arrangement.

As in the case of $SnCl_4$(bipy),[13,15] the four infrared-active ν(Sn–Cl) modes expected for *cis*-$SnCl_4I$ are not clearly resolved. We observe three of the modes at 335, 310, and 295 cm^{-1} which appear at higher energies than the corresponding bands reported for analogous bipy and phen complexes. In addition to the expected ligand absorption at 270 cm^{-1}, a sharp, medium-intensity band is found at 207 cm^{-1}. It is quite possible that this is an Sn–N stretching vibration similar to that reported at 202 and 181 cm^{-1} in the bipy and phen compounds.[13,15] This band would be expected to suffer a decrease in energy with increasing alkylation of the tin and is therefore not observed in any of the other complexes.

The number of Sn–C stretching modes should also be indicative of the geometry: one for a *trans*-R and two for a *cis*-R arrangement. The single strong ν(Sn–C) at 568 cm^{-1} found in $(CH_3)_2SnCl_2I$ further supports a *trans*-R geometry. When R = C_2H_5, C_3H_7, and C_4H_9, the absorption at 533 (m), 615 (w), and 625 (vw) cm^{-1}, respectively, is assigned to ν(Sn–C). The ν_{sym}(Sn–C), if observed at all for a *trans*-R arrangement, is expected to be very weak. The very weak shoulders at 485, 588, and 590 cm^{-1} noted when R = C_2H_5, C_3H_7, and C_4H_9, respectively, may be due to ν_{sym}(Sn–C) or solid-state splitting. The position and number of Sn–C absorptions reported for analogous complexes of phen and bipy are very similar.[13,15]

Pmr Spectra.—The pmr spectra of the prepared complexes are reported in Table I. The molecular weight of $(C_4H_9)_2SnCl_2I$ determined in chloroform, 458 (theoretical 462), demonstrates that these complexes remain as molecular species in solution. In all complexes, the ligand protons exhibit resonances at approximately 2.9 (singlet), 7.6 (doublet), and 8.4 ppm (doublet) which are assigned to the 2,9 methyls, 3,6 protons, and 4,5 protons, respectively. The *asym*-R geometry may be eliminated from consideration since only a single ligand methyl resonance is observed.

Electron donation to the tin on coordination has produced a deshielding of all ligand protons, the magnitude of which appears to be influenced by the inductive effect of the R groups attached to the tin. That all protons are not deshielded by the same amount may be the result of interaction of the *ortho* substituents with the bulky tin nucleus as proposed for the complex $(CH_3)_2SnCl_4L_2$ when L = 2,4-dimethylpicoline N-oxide.[8] A general deshielding of all ligand protons in compounds of the type $R_2SnCl_2L_2$, where L = 4-picoline[4] and 4-picoline N-oxide,[8] has also been reported. The coupling constant $J_{3,4}$ is insensitive to complexation and remains at 8.2 Hz.[10]

The alkyl groups attached to the tin (except CH_3) exhibit shielding on complex formation, again in agreement with an increased electron density on the tin *via* ligand donation. The greatest effect, however, is always observed on the terminal CH_3 group, with the smallest on the group directly bonded to the tin. This, as well as the marked deshielding observed when R = CH_3, may be explained by assuming a *trans*-R arrangement which is necessarily perpendicular to the naph-

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TABLE I

PROTON MAGNETIC RESONANCE DATA[a]

Compounds	Chemical shift positions (τ)					Coupling constants, Hz	
	2,7-CH_3	3,6-H[b]	4,5-H[b]	R group		$J_{Sn^{117}-H_a}$	$J_{Sn^{119}-H_a}$
				CH_3	CH_2		
I	7.24	2.72	2.00				
$SnCl_4I$	7.02	2.09	1.18				
$(CH_3)_2SnCl_2I$	7.08	2.43	1.59	8.70 (8.83)[c]		89	92
$(C_2H_5)_2SnCl_2I$	7.07	2.44	1.62	8.75 (8.53)	8.23 (8.22)	166	172
$(C_3H_7)_2SnCl_2I$	7.09	2.46	1.65	9.07 (8.88)	8.27 (8.16)		
$(C_4H_9)_2SnCl_2I$	7.10	2.46	1.63	9.15 (9.04)	9.05 (8.94), 8.19 (8.19)		
$(C_5H_{11})_2SnCl_2I$	7.11	2.47	1.66	9.21 (9.09)	8.75 (8.61), 8.23 (8.18)		
$(C_{12}H_{25})_2SnCl_2I$	7.15	2.59	1.80		8.77 (8.72)		

[a] Tetramethylsilane used as an internal standard in deuteriochloroform solutions for all spectra. [b] Doublet. [c] Values in parentheses are for appropriate uncomplexed R_2SnCl_2 resonances.

thyridine ring. Free rotation would allow the CH_3 groups on the end of the alkyl chains and the intermediate CH_2 groups to reside above the cloud of the heterocycle producing shielding, while a group directly attached to the tin would be in a deshielded area. This, in addition to the normal inductive effect of adding a coordinating ligand and the magnetic influence of the bulky tin atom, combine to govern the alkyl resonance position. The importance of neighbor anisotropy effects has also been clearly demonstrated in the $(C_2H_5)_nSnX_{4-n}$ system.[16]

Evidence in support of a linear R–Sn–R moiety may be derived by applying Kaesz' arguments[17] concerning the relationship between the magnitude of $J_{Sn^{117,119}-H}$ and the hybridization of tin bonding orbitals in compounds containing tin–methyl bonds. Table I lists the observed coupling constants for R_2SnCl_2I complexes where R = CH_3 and C_2H_5. A 33% s character for the methyl–tin bonding orbitals in $(CH_3)_2SnCl_2$ is obtained from the $J_{Sn^{117}-H}$ and $J_{Sn^{119}-H}$ values of 67 and 70 Hz, respectively. The analogous values for $(CH_3)_2SnCl_2I$ are found to be 89 and 92 Hz which correspond to 44% s character, suggesting a linear CH_3–Sn–CH_3 arrangement. The recent X-ray determination of the CH_3–Sn–CH_3 angle in $(CH_3)_2SnCl_2 \cdot 2DMSO$ to be 172.4°[18] while exhibiting $J_{Sn^{117,119}-H}$ values corresponding to 41% s character[19] justifies this argument.

The ethyl resonances of $(C_2H_5)_2SnCl_2I$ appear as an A_3B_2X system with $J_{Sn^{117,119}-A}$ clearly discernible as 166 and 172 Hz, respectively, while $J_{Sn^{117,119}-B}$, due to overlapping spectral features, may only be estimated to be 67 Hz. That J_{Sn-B} is smaller than J_{Sn-A} is typical of A_3B_2X spectra wherein X is a heavy element. Uncomplexed $(C_2H_5)_2SnCl_2$ exhibits $J_{Sn^{117,119}-A}$ and $J_{Sn^{117,119}-B}$ values of 125, 133 and 50, 52 Hz, respectively.[16]

Attempts to extend Kaesz' treatment[17] to ethyltin compounds have proven frustrating. The per cent s character estimated for these compounds differs depending on whether J_{Sn-A} or J_{Sn-B} is employed and yields values as much as 20% higher than similar methyltin compounds.[16] The dominating factor contributing to increases in the magnitude of J_{Sn-A} and J_{Sn-B} in the ethyl compounds has previously been ascribed as arising from an increase in the effective nuclear charge of the tin atom.[16] However, in the case of $(C_2H_5)_2SnCl_2I$, J_{Sn-A} and J_{Sn-B} have increased markedly from $(C_2H_5)_2SnCl_2$ while the effective nuclear charge of the tin has decreased. In the analogous 4-picoline complex, $J_{Sn^{117,119}-A}$ values are 155 and 161 Hz.[4] That complexation increases the coupling constants, decreases the effective nuclear charge, and presumably produces a linear R–Sn–R arrangement is worthy of note.

The similarity of spectral features of tin complexes of bipy, phen, and I is striking. This, in addition to stability in solution, indicates that four-member chelate ring formation in octahedral systems is not unfavorable in the absence of π-bonding interactions. Further studies of the complex behavior of I and other 1,8-naphthyridines with alkyl- and halogen-containing tin, lead, and germanium compounds are in progress.

Acknowledgment.—The author wishes to thank Mrs. K. L. Decker and Mr. R. L. Bodner for their help in obtaining analytical and spectral data.

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