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PMR AND THERMODYNAMIC STUDIES OF DIMETHYLTIN DICHLORIDE/PICOLINALDIMINE* ADDUCTS

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SUMMARY

Stable dimethyltin dichloride adducts with several picolinaldimines (C_5H_4-NCH=NR, R = CH_3, $C_6H_4OCH_3$-*p*, $C_6H_4CH_3$-*p*, C_6H_4Cl-*p*) have been isolated and the configurations in solution have been discussed on the basis of PMR spectra of the complexes. Equilibrium constants of the adducts in acetonitrile have been determined from the ^{119}Sn–CH_3 coupling constants of dimethyltin dichloride. Heats of complex formation in acetonitrile have also been measured by calorimetry, and thermodynamic parameters in the complex formation have been obtained.

INTRODUCTION

Several stable adducts of organotin(IV) halides with various nitrogen donors such as pyridine[1–4], picoline[3,5], 2,2′-bipyridine[4,6,10], 1,10-phenanthroline[6,7,10], 2,7-dimethyl-1,8-naphthyridine[11], picolin- and nicotinamides[12], 8-methoxyquinoline[13], aniline derivatives[14] and Schiff bases[15–19] have been prepared and characterized. However, few quantitative studies of these adducts in solution have been reported[8,9,13,14].

Recently PMR studies, particularly measurements of spin–spin coupling constants between the tin and methyl protons, have provided us with important electronic and structural information on methyltin(IV) halide adducts with Lewis bases[20,21]. Unfortunately, most of the dimethyltin dichloride adducts are practically insoluble in non-coordinating solvents, or they dissociate to some extent when dissolved in any solvent. Accordingly, there are only a few reports of PMR measurements[11,20] of undissociated alkyltin(IV) halide adducts but measurements under dissociating conditions have been more frequently reported[5,21–23].

Thermodynamic studies of dimethyltin dichloride adducts are also very few[3,8,9]. This is partly because of the great difficulty in determining thermodynamic parameters upon complex formation of dialkyltin(IV) dichloride with monodentate donors, in view of the existence of both penta- and hexa-coordinated tin(IV) complexes in solution. Previously we reported[9] thermodynamic parameters of 2,2′-bipyridine

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* Chem. Abstr. name: 2-formimidoylpyridine.

complexes of alkyltin(IV) chlorides. Kiefer and Van Dyke[3] recently reported a calorimetric study of organotin(IV) halides with nitrogen donors, but the measurements were not made in homogeneous solutions.

The imine nitrogen is also considered to have a strong ability to coordinate with metal halides[15–19]. In this paper we report the preparation of dimethyltin dichloride adducts with several picolinaldimines. Their configurations are discussed on the basis of their PMR spectra, and thermodynamic parameters of complex formation are determined by calorimetry.

EXPERIMENTAL

Materials

N-Methylpicolinaldimine. An excess of gaseous methylamine was condensed into a flask at about −30 °C, and picolinaldehyde was dropped into it. The mixture was then warmed slowly with stirring to room temperature. After dehydration by solid potassium hydroxide the solution was distilled under reduced pressure.

N-(p-substituted-phenyl)picolinaldimines. Equimolar mixtures of picolinaldehyde and *p*-substituted anilines were refluxed in ethanol for about 1 h. After the solvent was evacuated, the crude product obtained was purified by recrystallization from benzene or petroleum ether, or by distillation under reduced pressure.

Isolation of adducts of dimethyltin dichloride. A benzene solution of dimethyltin dichloride was mixed with an equimolar amount of picolinaldimines in benzene to give precipitates immediately, which were recrystallized from benzene/dichloromethane mixture or petroleum ether. The adducts are stable in air.

The m.p.'s and analytical data of picolinaldimines and their adducts with dimethyltin dichloride are summarized in Table 1.

PMR spectra

PMR spectra were obtained at 100 MHz with a Japan Electron Optics JNM-PS-100 spectrometer with a variable temperature probe and a temperature controller. The chemical shifts were measured relative to tetramethylsilane as an internal standard.

Calorimetric measurements

A calorimeter described elsewhere[9] was submerged in a thermostat at 25 ± 0.005° during the measurements. The reaction vessel was filled with 150.0 ml acetonitrile containing dimethyltin dichloride (10^{-2}–10^{-3} mol). A small glass ampoule containing a weighed acetonitrile solution of a picolinaldimine or a neat liquid ($\approx 10^{-3}$ mol) was supported in the vessel. Reaction was started by breaking the ampoule, and the heats of complex formation were measured in the same way as in the previous study[9]. Heats of dilution of picolinaldimines were measured separately in a similar way.

RESULTS AND DISCUSSION

PMR spectra

Fig. 1a shows the PMR spectrum of *N-p*-anisylpicolinaldimine (I) at a lower

TABLE 1

M.P. (B.P.) AND ANALYTICAL DATA OF PICOLINALDIMINES AND OF THEIR ADDUCTS WITH DIMETHYLTIN DICHLORIDE

Ligands and adducts	*M.p. (b.p.)* (°*C*)	*Analysis found (calcd.)* (%)		
		C	*H*	*N*
2-$C_5H_4NCH{=}NCH_3$ (L1)	(42/6 mmHg)	69.93 (69.96)	6.61 (6.71)	23.23 (23.32)
2-$C_5H_4NCH{=}NC_6H_4OCH_3$-*p* (L2)	40–41	73.36 (73.55)	5.63 (5.71)	13.11 (13.20)
2-$C_5H_4NCH{=}NC_6H_4CH_3$-*p* (L3)	57.5–59	79.31 (79.55)	6.08 (6.18)	14.00 (14.28)
2-$C_5H_4NCH{=}NC_6H_4Cl$-*p* (L4)	68–69	66.56 (66.51)	4.00 (4.20)	12.85 (12.93)
$(CH_3)_2SnCl_2 \cdot$ L1	160 (decomp.)	31.88 (31.80)	4.26 (4.15)	8.44 (8.25)
$(CH_3)_2SnCl_2 \cdot$ L2	187–187.5	41.73 (41.71)	4.02 (4.21)	6.38 (6.49)
$(CH_3)_2SnCl_2 \cdot$ L3	192	43.01 (43.31)	4.29 (4.37)	6.58 (6.74)
$(CH_3)_2SnCl_2 \cdot$ L4	187	38.51 (38.53)	3.51 (3.47)	6.79 (6.42)

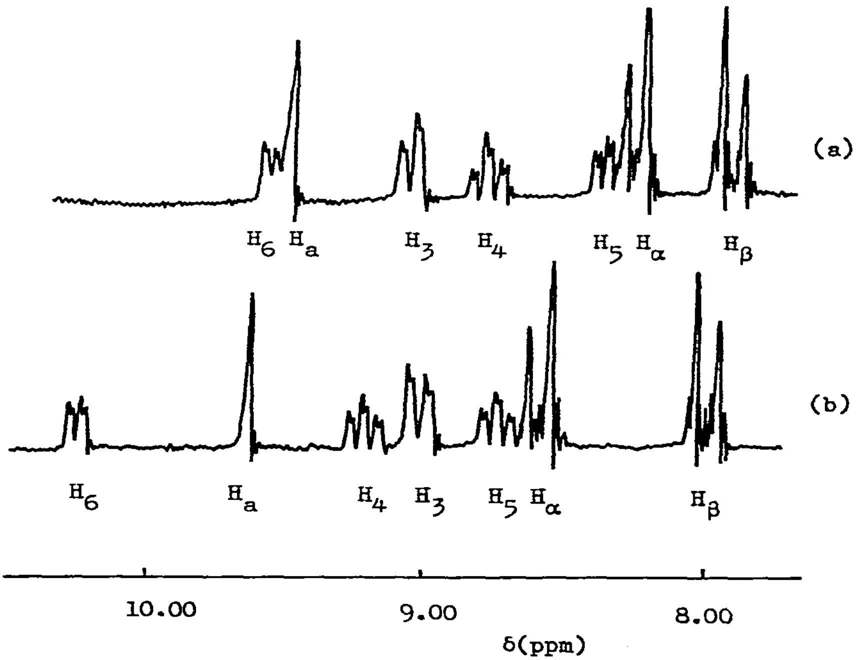


Fig. 1. PMR spectra of N-*p*-anisylpicolinaldimine and its complex with dimethyltin dichloride in the region of phenyl and pyridine protons, in acetonitrile at 21°.

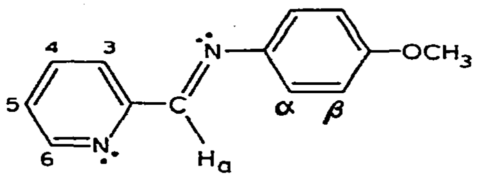
TABLE 2

PMR DATA OF PICOLINALDIMINES ($C_5H_4NCH{=}NR$) AND OF THEIR ADDUCTS OF DIMETHYLTIN DICHLORIDE IN ACETONITRILE AT 21°

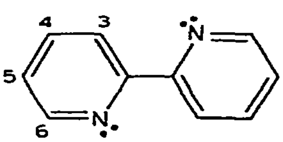
Compounds	*Chemical shifts, δ (ppm)*									*Coupling constants (Hz)*	
	3-*H*	4-*H*	5-*H*	6-*H*	H_a	H_α	H_0	H_x	Sn–CH_3	$J(^{119}Sn{-}CH_3)$	$J(^{117/119}Sn{-}N{=}CH{-})$[b]
Picolinaldimines (L)											
R = CH_3	7.94	7.77	7.34	8.60	8.34			3.50[c]			
$C_6H_4OCH_3$-*p*	8.04	7.75	7.34	8.56	8.50	7.26	6.94	3.82[d]			
$C_6H_4CH_3$-*p*	8.03	7.74	7.30	8.55	8.45	7.12	7.12	2.38[e]			
C_6H_4Cl-*p*	8.05	7.77	7.33	8.58	8.44	7.19	7.37				
Dimethyltin dichloride									1.19	83.4	
$(CH_3)_2SnCl_2 \cdot L$											
R = CH_3	7.99	8.27	7.83	9.21	8.65			3.74[c]	0.93	114.6	16
	(−0.05)[a]	(−0.50)	(−0.49)	(−0.61)	(−0.31)			(−0.24)	(+0.26)		
$C_6H_4OCH_3$-*p*	8.01	8.21	7.76	9.27	8.67	7.61	7.01	3.89[d]	1.04	111.6	19
	(+0.03)	(−0.46)	(−0.42)	(−0.71)	(−0.17)	(−0.35)	(−0.07)	(−0.07)	(+0.15)		
$C_6H_4CH_3$-*p*	7.98	8.19	7.75	9.22	8.63	7.43	7.26	2.43[e]	1.07	111.6	18
	(+0.05)	(−0.45)	(−0.45)	(−0.67)	(−0.18)	(−0.31)	(−0.14)	(−0.05)	(+0.12)		
C_6H_4Cl-*p*	8.03	8.21	7.73	9.23	8.66	7.49	7.49		1.10	111.5	18
	(+0.02)	(−0.44)	(−0.40)	(−0.65)	(−0.22)	(−0.30)	(−0.12)		(+0.09)		

[a] The values in parentheses are $(\delta_{free} - \delta_{complexed})$. [b] Values in dichloromethane at −50°. [c] NCH_3. [d] OCH_3. [e] $C_6H_4CH_3$.

field in acetonitrile at room temperature. The 3-H and 6-H proton signals occur at very low field. This may be due to paramagnetic anisotropies of the pyridine and imine nitrogen atoms, located close to these protons. The configuration of the free picolinaldimine with respect to the nitrogen atoms would therefore be almost the same as that of 2,2′-bipyridine, which is well known to be the *trans*-structure (II)[24–26].



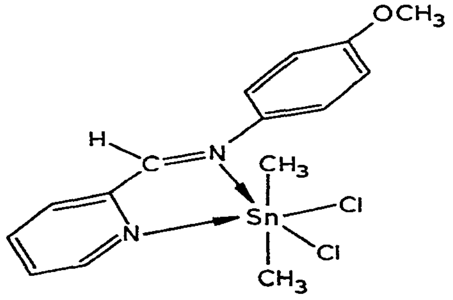
(I)



(II)

The paramagnetic anisotropic effect of these kinds of nitrogen atoms has already been confirmed in the PMR spectra of pyridine[27–30] and 2,2′-bipyridine[29,31,32]. PMR spectra of the other picolinaldimines at lower fields indicate similar behaviour.

In Fig. 1b are illustrated low-field shifts of the ring protons of the ligand upon complex formation with dimethyltin dichloride. The 3-H signal, however, is virtually unshifted. This is due to the resultant of two mutually opposite effects; a low-field shift caused by the inductive effect and a high-field shift caused by disappearance of the paramagnetic effect of the imine nitrogen atom upon coordination, when (I) takes the *cis*-configuration with respect to the nitrogen atom (III). These two similar effects may also be expected to influence the 6-H signal. However, this signal shifts to a much lower field on coordination. Such a large low-field shift of protons attached to carbons adjacent to the nitrogen was also observed in 4-picoline dialkyltin dichloride[5], -boron trihalide adducts[33] and platinum halide complexes[34]. This is considered to be due to some paramagnetic effect of metal halides. The proton chemical shifts of several picolinaldimines and of their adducts with dimethyltin dichloride are shown in Table 2. Inspection of Table 2 reveals that the larger low-field shift may be related to the stronger coordination, as will be discussed below. In addition, in Table 2 are summarized the spin–spin coupling constants between the methyl protons and the tin nucleus in the dimethyltin moiety of the adducts. The large J values (111–115 Hz)



(III)

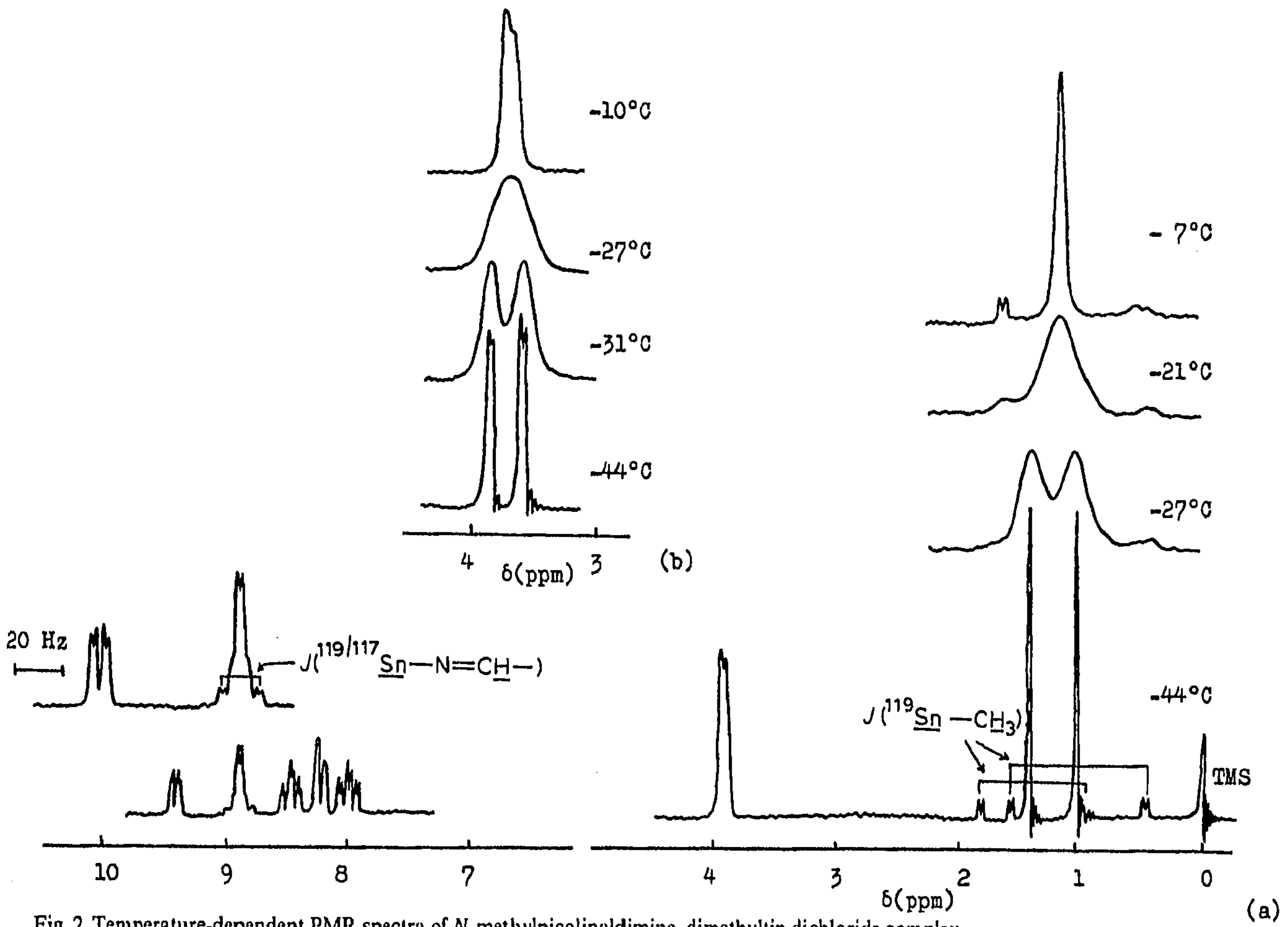
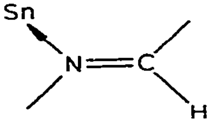


Fig. 2. Temperature-dependent PMR spectra of *N*-methylpicolinaldimine-dimethyltin dichloride complex in the presence of an excess amount of (a) dimethyltin dichloride and (b) the ligand, in dichloromethane.

suggest (but do not prove) the linear C–Sn–C moiety[35–37], as is shown in (III). In the far-infrared spectra of the *N*-methylpicolinaldimine complex the appearance of only one strong ν(Sn–C) band at 575 cm^{-1} and two intense ν(Sn–Cl) bands at 253 and 240 cm^{-1} also supports the structure (III). In the other three complexes, the regions of ν(Sn–C) and ν(Sn–Cl) are obscured by ligand vibration bands.

Fig. 2a depicts the temperature dependence of the Sn–CH_3 signals of dimethyltin dichloride in the presence of about a half amount of *N*-methylpicolinaldimine in dichloromethane. At room temperature a sharp signal is observed. However, the signal is broadened with lowering temperature and at −40° two signals, the lower field signal with a $J(^{119}$Sn–$CH_3)$ value of 74 Hz and the higher signal with a J value of 110 Hz, are observed. The former is assigned to free dimethyltin dichloride and the latter to the complex. This shows that the rate of exchange between free and complexed dimethyltin dichloride is slow enough to be measured at the PMR time-scale because of the strong coordination bond. This is the first experiment in which exchanging free and complexed organotin(IV) halides were observed separately, as far as we know. In the system containing an excess of *N*-methylpicolinaldimine the exchange between free and complexed ligands is also observed (see Fig. 2b), and the coalescence temperature is close to that of the Sn-CH_3 signals in the presence of a lesser amount of the ligand.

At a low temperature the spin–spin coupling between the tin and the H_a proton is observed, as is shown in Fig. 2a. This is also evidence for the existence of coordination of the imine nitrogen to the tin atom. This is not, however, apparent above the coalescence temperature on the Sn–CH_3 signals even with an excess amount of dimethyltin dichloride. In other *N*-arylpicolinaldimine complexes the similar spin–spin interaction is observed (see Table 2). These are also the first observations of the spin–spin coupling between the tin and ligand protons in tin(IV) halide adducts. The couplings between the tin and ligand protons through the nitrogen coordination bond were previously observed in the Sn^{IV} complexes of Schiff bases obtained from salicylaldehyde and *o*-aminophenol[38], although they are not addition compounds. The Schiff base complexes have the similar skeleton (IV) of the coupling nuclei to the picolinaldimines, and the coupling constants are larger in the former than in the latter. On the other hand, in the *N*-methylpicolinaldimine complex the spin–spin interaction of the tin nuclei with the *N*-methyl protons was not observed, while that between the tin and the *N*-methylene protons was observed in [bis(salicylaldehyde)ethylenediaminato]dichlorotin(IV)[39].



(IV)

Equilibrium constant, K, of the adduct formation

Figure 3 shows the $J(^{119}$Sn–$CH_3)$ values of dimethyltin dichloride with varying amounts of several picolinaldimines in acetonitrile. In the following equilibrium:

$$(CH_3)_2SnCl_2 + L \rightleftharpoons (CH_3)_2SnCl_2 \cdot L$$

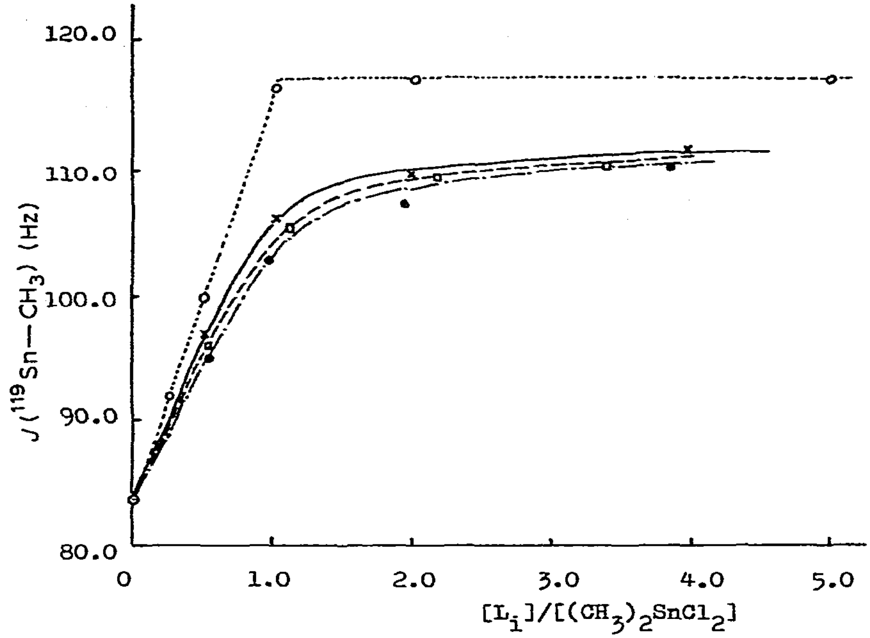


Fig. 3. Plots of the $J(^{119}Sn–CH_3)$ value of $(CH_3)_2SnCl_2$ ($4.0–7.0 \times 10^{-2}$ mol/l) against $[L_i]/[(CH_3)_2SnCl_2]$ in acetonitrile. ○, L1 = $C_5H_4NCH{=}NCH_3$; ×, L2 = $C_5H_4NCH{=}NC_6H_4OCH_3$-*p*; □, L3 = $C_5H_4NCH{=}NC_6H_4CH_3$-*p*; ●, L4 = $C_5H_4NCH{=}NC_6H_4Cl$-*p*; observed values. ······, L1; ————, L2; – – – –, L3; —·—·—, L4; calculated values.

the observed $J(^{119}Sn–CH_3)$ value, J_o, is derived from J_f and J_c values of free and complexed dimethyltin dichlorides, respectively, using the following equation;

$$J_o = x_f \cdot J_f + x_c \cdot J_c$$

where x_f and x_c are mole fractions of the free and complexed species, respectively. J_f is measured to be 83.4 Hz in acetonitrile, and J_c was estimated by extrapolation to an infinitely large excess of the ligand in solution. J_o values were calculated by assuming an appropriate K and by using a trial and error method until the values fitted those observed. The K values determined are summarized in Table 3. The K value of the *N*-methylpicolinaldimine adduct is too large to be determined precisely.

TABLE 3

EQUILIBRIUM CONSTANTS OF THE REACTION, $(CH_3)_2SnCl_2 + L \rightleftharpoons (CH_3)_2SnCl_2 \cdot L$, IN ACETONITRILE AT 25°

L	log *K*
$C_5H_4NCH{=}NCH_3$	>5
$C_5H_4NCH{=}NC_6H_4OCH_3$-*p*	2.60 ± 0.05
$C_5H_4NCH{=}NC_6H_4CH_3$-*p*	2.25 ± 0.05
$C_5H_4NCH{=}NC_6H_4Cl$-*p*	2.08 ± 0.05
2,2′-Bipyridine	3.30 ± 0.02 (ref. 9)

K values obtained are sensitive to the p-substituents attached to the nitrogen atom; a more electron-donating group increases the stability of the adduct.

Enthalpy change, ΔH, of the adduct formation

The experimental results obtained by calorimetry are shown in Table 4. The N-(p-chlorophenyl)picolinaldimine complex is unstable in acetonitrile and the precise calorimetric measurements did not succeed. Using the ΔG values derived from equilibrium constants and the ΔH obtained, ΔS values were calculated. They are summarized in Table 5. A more electron-donating substituent attached to the imine-

TABLE 4

CALORIMETRIC EXPERIMENTS USING VARYING RATIOS OF DIMETHYLTIN DICHLORIDE (A) TO PICOLINALDIMINES (L) IN ACETONITRILE AT 25°

L	10^3C_A (*mol*)	10^3C_L (*mol*)	h_0 (*cal*)	h (*cal*)	n	$-\Delta H$ (*kcal·mol*$^{-1}$)
$C_5H_4NCH{=}NCH_3$						
	9.757	1.162	14.66	15.52	1.00	13.35
	6.942	1.278	16.64	17.51	1.00	13.70
	5.897	1.176	15.34	16.21	1.00	13.78
	5.000	1.421	18.21	19.09	1.00	13.43
					$-\Delta H_{av.}=$	13.57 ± 0.18
$C_5H_4NCH{=}NC_6H_4OCH_3$-p						
	6.285	0.828	8.51	8.63	0.947	11.00
	5.096	0.856	8.34	8.47	0.926	10.69
	2.325	0.817	6.36	6.48	0.830	9.56
					$-\Delta H_{av.}=$	10.42 ± 0.62
$C_5H_4NCH{=}NC_6H_4CH_3$-p						
	8.395	0.527	4.44	4.60	0.912	9.57
	5.610	0.561	4.65	4.81	0.861	9.96
	3.970	0.500	3.56	3.68	0.826	8.91
	2.800	0.561	3.42	3.58	0.741	8.61
					$-\Delta H_{av.}=$	9.26 ± 0.53

C_A, initial concentrations of dimethyltin dichloride; C_L, initial concentrations of picolinaldimines; h_0, heats evolved; h, heats after correction by heats of dilution of ligands; n, ratios [Complex]/C_L.

TABLE 5

THERMODYNAMIC DATA FOR THE REACTION, $(CH_3)_2SnCl_2 + L \rightleftarrows (CH_3)_2SnCl_2 \cdot L$, IN ACETONITRILE AT 25°

$C_5H_4NCH{=}NR$ (*L*)	$-\Delta G$ (kcal·mol^{-1})	$-\Delta H$ (kcal·mol^{-1})	$-\Delta S$ (kcal·mol^{-1}·deg^{-1})
R = CH_3	>7	13.57 ± 0.18	<22
$C_6H_4OCH_3$-p	3.55 ± 0.03	10.42 ± 0.62	23.0 ± 2.3
$C_6H_4CH_3$-p	3.07 ± 0.03	9.26 ± 0.53	20.8 ± 1.7
2,2′-Bipyridine (ref. 9)	4.50 ± 0.02	11.88 ± 0.01	24.8 ± 0.2

nitrogen increases the ΔH value, as is seen in K values, and the substitution of the methyl group on the imine nitrogen by aryl groups considerably decreases both the ΔH and ΔG values. This may be due to some steric hindrance of the aryl groups. It is also seen from Table 5 that the ΔH terms contribute greatly to the ΔG terms. The ΔH values obtained here are as large as those of 2,2'-bipyridine[9] and bis(pyridine) complexes[3], indicating the strong coordinating ability of the imine nitrogen.

As shown by the PMR spectra, *trans*-picolinaldimines would rotate by about 180° around the pyridine–imine bond upon complex formation to form the chelate ring as in the case of 2,2'-bipyridine. The ΔS values obtained here are almost consistent with the value (24.8 $\text{kcal}\cdot\text{mol}^{-1}\cdot\text{deg}^{-1}$) of 2,2'-bipyridine complex with dimethyltin dichloride[9], and the negative entropy changes on complex formation may be mainly due to the decrease of translational and rotational freedom of the ligands. When the complexes are formed, increasing freedom of acetonitrile molecules which were associated with dimethyltin dichloride would also appreciably contribute to the ΔS value, as pointed out previously.

REFERENCES

1 I. R. Beattie and G. P. McQuillan, *J. Chem. Soc.*, (1963) 1519.
2 T. Tanaka, Y. Matsumura, R. Okawara, Y. Musha and S. Kinumaki, *Bull. Chem. Soc. Jap.*, 41 (1968) 1497.
3 E. W. Kiefer and C. H. Van Dyke, *Anal. Calorimetry*, 2 (1970) 239.
4 J. P. Clark and C. J. Wilkins, *J. Chem. Soc. A*, (1966) 871.
5 D. G. Hendricker, *Inorg. Nucl. Chem. Lett.*, 5 (1969) 115.
6 D. L. Alleston and A. G. Davis, *J. Chem. Soc.*, (1962) 2050.
7 T. Tanaka, M. Komura, Y. Kawasaki and R. Okawara, *J. Organometal. Chem.*, 1 (1964) 484.
8 M. Komura, Y. Kawasaki, T. Tanaka and R. Okawara, *J. Organometal. Chem.*, 4 (1965) 308.
9 G. Matsubayashi, Y. Kawasaki, T. Tanaka and R. Okawara, *J. Inorg. Nucl. Chem.*, 28 (1966) 2937.
10 R. J. H. Clark and C. S. Williams, *Spectrochim. Acta, Part A*, 21 (1965) 1861.
11 D. G. Hendricker, *Inorg. Chem.*, 8 (1969) 2328.
12 G. Matsubayashi, M. Hiroshima and T. Tanaka, *J. Inorg. Nucl. Chem.*, 33 (1969) 3787.
13 Y. Kawasaki, T. Suda and R. Okawara, to be published.
14 J. L. Wardell, *J. Organometal. Chem.*, 9 (1967) 89; 10 (1967) 53.
15 G. Faraglia, F. Maggio, R. Cefalù, R. Bosco and R. Barbieri, *Inorg. Nucl. Chem. Lett.*, 5 (1969) 177.
16 R. Barbieri, R. Cefalù, S. S. Chandra, and R. H. Herber, *J. Organometal. Chem.*, 32 (1971) 97.
17 R. Cefalù, L. Pellerito, and R. Barbieri, *J. Organometal. Chem.*, 32 (1971) 107.
18 K. Kawakami, M. Miya-uchi and T. Tanaka, *J. Inorg. Nucl. Chem.*, 33 (1971) 3773.
19 P. J. Smith and D. Dodd, *J. Organometal. Chem.*, 32 (1971) 195.
20 T. F. Bolles and R. S. Drago, *J. Amer. Chem. Soc.*, 88 (1966) 3921, 5730.
21 G. Matsubayashi, Y. Kawasaki, T. Tanaka and R. Okawara, *Bull. Chem. Soc. Jap.*, 40 (1967) 1566.
22 W. Kitching, *Tetrahedron Lett.*, (1966) 3689.
23 W. Kitching and V. G. K. Das, *Aust. J. Chem.*, 21 (1968) 2401.
24 F. Bertinotti, A. M. Liquori and R. Parisi, *Gazz. Chim. Ital.*, 86 (1956) 893.
25 L. L. Merritt and E. D. Schroeder, *Acta Crystallogr.*, 9 (1956) 801.
26 K. Nakamoto, *J. Phys. Chem.*, 64 (1960) 1420.
27 J. I. Musher, *J. Chem. Phys.*, 37 (1962) 34.
28 V. S. M. Gil and J. N. Murrell, *Trans. Faraday Soc.*, 60 (1964) 248.
29 T. McL. Spotswood and C. I. Tanzer, *Tetrahedron Lett.*, (1967) 911.
30 J. W. Emsley, *J. Chem. Phys.*, 46 (1968) 4731.
31 C. I. Calder, T. McL. Spotswood and C. I. Tanzer, *Aust. J. Chem.*, 20 (1967) 1195.
32 T. McL. Spotswood and C. I. Tanzer, *Aust. J. Chem.*, 20 (1967) 1227.
33 A. Fratiello and R. E. Shuster, *Inorg. Chem.*, 7 (1968) 1581.

34 M. Orchin and P. J. Schmidt, *Inorg. Chim. Acta Rev.*, 2 (1968) 123.
35 J. R. Holmes and H. D. Kaesz, *J. Amer. Chem. Soc.*, 83 (1961) 3903.
36 M. M. McGrady and R. S. Tobias, *J. Amer. Chem. Soc.*, 87 (1965) 1909.
37 T. Tanaka, *Inorg. Chim. Acta*, 1 (1967) 217.
38 K. Kawakami and T. Tanaka, *J. Organometal. Chem.*, 49 (1973) 409.
39 A. van den Bergen, R. J. Cozens and K. S. Murray, *J. Chem. Soc. A*, (1970) 3060.