Contribution from the Department of Chemistry,
State University of New York at Albany, Albany, New York 12222

Tin-119m Mössbauer, Infrared, Nuclear Magnetic Resonance, Equilibrium, and Thermodynamic Measurements on Complexes of Dimethyltin Dichloride with Substituted 1,10-Phenanthrolines and 2,2'-Bipyridines

W. D. HONNICK, M. C. HUGHES, C. D. SCHAEFFER, Jr., and J. J. ZUCKERMAN*

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Ten substituted 1,10-phenanthrolines and two substituted 2,2'-bipyridines have been used to complex dimethyltin dichloride in 1:1 adducts. Tin-119m Mössbauer quadrupole splitting data (3.8–4.1 ± 0.12 mm/s) specify a *trans*-$(CH_3)_2Sn$ configuration, and far-infrared spectral data confirm these conclusions. The isomer shifts are all within experimental error of one another (1.43 ± 0.06 mm/s). Ligand infrared bands are generally raised to higher frequencies on complexation. Formation constants and thermodynamic values are determined for eight to ten temperatures between 25 and 65 °C in acetonitrile by a uv spectroscopic method. A second isosbestic point is observed at very high organotin chloride to ligand ratios and is rationalized in terms of the formation of ligand-complexed dimethyltin dication species. The formation constants fall roughly in the same order as the pK_a values for the monoprotonated organic ligands or their tris iron(II) and copper(II) complexes in aqueous media: 5-CH_3phen > 5-C_6H_5phen > 5-Cl(phen) > 5-Br(phen) > 5-NO_2phen > 4,4'-$(CH_3)_2$bpy > bpy. All of the entropy changes measured are negative, with the most negative associated with the most exothermic processes; e.g., the formation of the 5-CH_3phen adduct is the most exothermic and is productive of the most order in the system. The formation of the 5-NO_2phen complex is least exothermic. The NMR $|J(^{119}Sn-C-^{1}H)|$ values for the phen adducts fall roughly in the same order as the enthalpies. Redetermination of the thermodynamic values in undried acetonitrile yields lower entropy changes and data more similar to those in the literature for $(CH_3)_2SnCl_2$·bpy.

Introduction

Since the first reports[1,2] in 1961, many workers have studied the chelate complexes formed between the diimine ligands 1,10-phenanthroline (phen) and 2,2'-bipyridine (bpy) and organic[1–26] and inorganic tin halides[27–34] and organotin heterocycles.[35–40] The complexes are monomeric 1:1 adducts with the tin moiety.[41]

In all previous studies save one,[13] complexes of unsubstituted phen and bpy with various tin-bearing Lewis acids have been investigated. In this paper we report tin-119m Mössbauer, infrared, NMR, equilibrium, and thermodynamic data on complexes of a single organotin compound, dimethyltin dichloride, with series of substituted phen's and bpy's in order to determine the effects of the ligand substituents on the nature of the complexes and their formation.

Experimental Section

Dimethyltin dichloride (M&T Chemicals) and the ligands listed in Table I (G. Frederick Smith Chemical Co.) were used as received. Acetonitrile (Fisher Chemical Co. AN reagent grade) was dried over molecular sieves and was refluxed over and distilled from calcium hydride.

The solid complexes precipitated on mixing saturated solutions of dimethyltin dichloride and the ligand in warm, anhydrous ethanol. The mixtures were chilled and filtered, and the precipitates washed with anhydrous ether and dried in a desiccator (not under vacuum). The complex with 5-nitrophenanthroline discolored on exposure to light. The other complexes were stable to air and moisture and were not photosensitive.

Mössbauer spectra were recorded on our cam-drive, constant-acceleration spectrometer at 77 K vs. a $Ba^{119m}SnO_3$ (New England Nuclear Corp.) source. The spectrometer and curve-fitting procedure have been previously described.[42]

Infrared spectra were recorded on a Beckman IR-12 spectrometer. Spectra in the 650–200-cm^{-1} range were run on samples in Nujol mulls held between polyethylene sheets. Spectra from 2000 to 400 cm^{-1} were run as KBr pellets.

Ultraviolet spectra were run on a Cary Model 14 spectrophotometer equipped with circulating-water cell compartments. Temperature was controlled to ±0.2 °C. Thermodynamic measurements were made over a temperature range of ca. 40 °C between 25 and 65 °C.

Both the ligands and complexes absorb in the ultraviolet region between 300 and 260 nm, with the complex absorbance maximizing at 10–15 nm longer wavelengths than that of the free ligand. Dimethyltin dichloride does not absorb appreciably in this region (molar absorptivity <1).

Table I. Melting Points and Spectrophotometric Data for Me_2SnCl_2·L Complexes

L	Complex mp, °C	Complex λ_{max}, nm[a]
1,10-Phenanthroline	282–284[b]	270 (3.1 × 10^4)
5,Methyl-1,10-phenanthroline	214–216	275 (3.9 × 10^4)
5,6-Dimethyl-1,10-phenanthroline	300–304 dec	c
4,7-Dimethyl-1,10-phenanthroline	268–271 dec	270
3,4,7,8-Tetramethyl-1,10-phenanthroline	267–270 dec	277
5-Phenyl-1,10-phenanthroline	268–270 dec	278 (3.2 × 10^4)
4,7-Diphenyl-1,10-phenanthroline	250–254 dec	c
5-Chloro-1,10-phenanthroline	232–234	273 (3.5 × 10^4)
5-Bromo1,10-phenanthroline	241–243	c
5-Nitro-1,10-phenanthroline	244–247 dec	270 (2.8 × 10^4)
2,2'-Bipyridine	237–239[d]	303 (1.6 × 10^4)
4,4'-Dimethyl-2,2'-bipyridine	280–282	303 (1.6 × 10^4)

[a] Extinction coefficients (where measured) in parentheses. Values are for acetonitrile solution. [b] Melting point listed as 284 °C in ref 5 and as 200 °C dec in ref 6. [c] Not determined. [d] Melting point listed as 250 °C in ref 5 and as 232–233 °C in ref 6.

At the concentrations normally employed ([L] ≈ 10^{-5} M, $[(CH_3)_2SnCl_2] \approx 10^{-5}$–$10^{-3}$ M), spectra were run vs. an acetonitrile blank. For $[(CH_3)_2SnCl_2] > 10^{-2}$ M, a dimethyltin dichloride blank with concentration equal to the total organotin chloride concentration was used. Fresh organotin chloride and ligand solutions were prepared for each series of measurements using freshly distilled acetonitrile. Stock solutions of 10^{-3} M were diluted to make the working solutions.

Equilibrium constants were calculated using a least-squares curve-fitting program based upon the equation

$$A_t = \epsilon_C C_{eq} + \epsilon_B B_{eq} \qquad (1)$$

where A_t is the total absorbance of the solution at equilibrium at a temperature T, ϵ_C and ϵ_B are the extinction coefficients of the complex and the free ligand, respectively, C_{eq} is the equilibrium complex concentration, and B_{eq} is the free ligand concentration at equilibrium. These latter concentrations, C_{eq} and B_{eq}, for a given solution at temperature T, are constant over a range of wavelengths, while A_t and the extinction coefficients are known variables, the latter derived from solutions containing only the free ligand or complex. The total absorbance, A_t, was measured, and C_{eq} and B_{eq} were calculated using a least-squares curve-fitting procedure. Equilibrium constants were calculated for eight to ten temperatures over the range employed, and $\Delta G°$, $\Delta S°$, and $\Delta H°$ were computed and tabulated at 298 K by

Table II. Tin-119m Mössbauer Parameters for $(CH_3)_2SnCl_2$ Complexes of Substituted Phenanthroline and Bipyridyl Derivatives[a]

Complex	IS[b]	QS[c]	Γ_1[b]	Γ_2[b]
$(CH_3)_2SnCl_2$·phen	1.42	4.15	1.27	1.18
·5-CH_3phen	1.42	3.93	1.29	1.27
·5,6$(CH_3)_2$phen	1.42	3.99	1.74	1.66
·4,7-$(CH_3)_2$phen	1.37	3.96	1.18	1.11
·3,4,7,8-$(CH_3)_4$phen	1.38	3.82	1.40	1.31
·5-C_6H_5phen	1.40	3.83	1.20	1.19
·4,7-$(C_6H_5)_2$phen	1.49	4.07	1.06	1.12
·5-Cl(phen)	1.39	4.07	1.09	1.19
·5-Br(phen)	1.45	3.92	1.28	1.20
·5-NO_2phen	1.38	4.04	1.34	1.27
·bpy	1.45	4.03	1.22	1.21
·4,4'-$(CH_3)_2$-bpy	1.36	3.96	1.08	1.16

[a] Recorded at 77 K vs. a $Ba^{119m}SnO_3$ (New England Nuclear Corp.) source at ambient temperature. [b] ±0.06 mm/s. [c] ±0.12 mm/s.

standard methods. In the computation it is assumed that only ligand and complex absorb in the region of interest (300–250 nm) since dimethyltin dichloride is transparent in that range. The extinction coefficients, ϵ, of the ligands and complexes were ca. 10^3–10^4, but only 10^{-1}–1 for dimethyltin dichloride. Beer's law was assumed to hold over this concentration range, and ϵ values were assumed to be constant with temperature in the 25–65 °C range. It was further assumed that, at the concentration ratio at which the absorbance of the complex was a maximum, the complex was the only species to absorb significantly. Since there was a considerable range of ratios at which ϵ_C was relatively constant, [(e.g., for $(CH_3)_2SnCl_2$·phen the ϵ_C value was constant for organotin chloride:phen ratios of ca. 20:1 to 10^3:1)] and the magnitudes of the ratios were large, it was assumed that no significant error was introduced by this procedure.

At the organotin chloride:ligand ratios used to calculate the thermodynamic parameters, both ligand and complex are present and absorb. Thus a least-squares curve-fit to eq 1 was used in the form

$$y = ax + bz \tag{2}$$

Over a range of wavelengths at constant temperature T, C_{eq} and B_{eq} are constant, but unknown, while A_t, ϵ_C, and ϵ_B are variable and known. The least-squares results were used to compute C_{eq} and B_{eq}. The equilibrium concentration of the free organotin chloride was calculated as

$$[(CH_3)_2SnCl_2]_{eq} = [(CH_3)_2SnCl_2]_{initial} - C_{eq} \tag{3}$$

Then

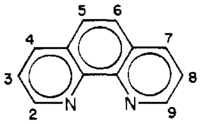
$$K_{eq} = C_{eq}/[(CH_3)_2SnCl_2]_{eq}B_{eq} \tag{4}$$

and $\Delta G = -RT \ln K_{eq}$. The ΔH and ΔS values were calculated from the plot of ln K vs. $1/T$ and listed at 298 K.

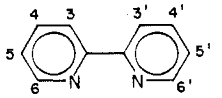
NMR spectra were recorded on Varian A-60A and HA-100D instruments in CH_2Cl_2.

Results and Discussion

The numbering scheme for the substituted phen and bpy ligands is indicated in their structures.



phen



bpy

Tin-119m Mössbauer Data. Mössbauer spectra of a number of organotin complexes of phen and bpy have been recorded.[11,15,18-22,30-43] The isomer shift (IS) and quadrupole splitting (QS) data for the unsubstituted phen and bpy complexes of dimethyltin dichloride which are listed in Table II are in excellent agreement with those previously reported.[44,45] The similarity of the data for all 12 complexes studied suggests that they are isostructural and that the change of the ligand substituents does not alter the electronic situation at the tin atom to a strong degree.[46] The IS data fall in the range 1.43 ± 0.06 mm/s; i.e., all are within experimental error.

Table III. Far-Infrared Bands in the Spectra of phen and bpy Derivatives and Their Complexes (cm^{-1})[a]

phen	L[b]	409 w, m, 259 w, sh, 242 s
	C[c]	580 m,[e] 419 w, m, 280 w, 249 s, br,[f] 236 sh
5-CH_3phen	L	565 w, 410 w, m, 247 w
	C	568 m,[e] 420 w, m, 276 sh, 263 s, br,[f] 246 sh
5,6-$(CH_3)_2$phen	L	542 w, 416 w, m, 253 vw
	C	574 w, m,[e] 546 w, 430 m, 290 w, 240 s, br[f]
4,7-$(CH_3)_2$phen	L	576 vw, 529 m, sh, 524 m, sh, 501 w, 487 w, 453 w, 280 m
	C	568 m,[e] 547 m, 541 m, 515 w, 485 w, 463 w, 245 s, br[f]
$(CH_3)_4$phen	L	570 w, 527 w, 515 w, 478 w, 458 w, 295 w, 260 w
	C	573 vw, 560 m,[e] 530 w, 464 w, 251 s, br[f]
5-C_6H_5phen	L	411 w, 277 w
	C	569 m,[e] 422 m, 251 s, br,[f] 209 w
4,7-$(C_6H_5)_2$phen	L	596 w, 575 w, 543 w, 472 w, 304 w, 288 w
	C	599 w, 575 m, 548 m,[e] 492 w, 472 w, 445 w, 244 s, br[f]
5-Cl(phen)	L	570 w, 414 m, 301 w, 279 w, 250 w, 222 w
	C	572 m,[e] 421 m, 274 w, 240 s, br[f]
5-Br(phen)	L	595 w, 560 w, 434 w, 410 w, 279 w, 250 w, 222 w
	C	578 m,[e] 421 m, 314 w, 300 w, 240 s, br[f]
5-NO_2phen	L	412 w, 280 w, 242 w
	C	576 m,[e] 422 m, 337 w, 249 s, br[f]
bpy	L[d]	398 m
	C	572 m,[e] 427 w, 410 w, 243 s, br,[f] 215 w
4,4'-$(CH_3)_2$bpy	L	524 sh, 516 s, 415 m
	C	572 m,[e] 518 m, 422 w, 253 s, br[f]

[a] Recorded as Nujol mulls. [b] Free ligand. [c] Complex. [d] Taken from ref 56. [e] ν(Sn–C). [f] ν(Sn–Cl).

Three stereochemistries are possible for the complexes, one with *trans*-$(CH_3)_2Sn$ groups requiring a *cis*-Cl_2Sn moiety given the chelating N_2Sn group present (idealized C_{2v} symmetry) and a second with a *cis*-$(CH_3)_2Sn$ group but a *trans*-Cl_2Sn moiety (also C_{2v}); a third possibility would have all three pairs of atoms about the octahedron arranged cis (dissymmetric).

The QS parameter has, with the application of the results of point-charge calculations,[47] proved useful in distinguishing *cis*- and *trans*-R_2Sn configurations in complexes with O_h geometries. In fact the dimethyltin dichloride complexes of phen and bpy were used by Fitzsimmons et al.[48,49] in 1969 in the first illustration of the power of the method. It was shown with those examples that *trans*-R_2Sn groups give rise to QS values of ca. 4 mm/s while complexes with cis configurations exhibit splittings only half as large. Thus the simple phen and bpy complexes of dimethyltin dichloride were shown to contain *trans*-$(CH_3)_2Sn$ groups,[48,49] and we conclude that the substituted derivatives in Table I whose QS values lie in the range 3.82–4.15 ± 0.12 mm/s are isostructural.

Recent calculations of the partial electric field gradients created by a number of groups bonded to tin suggest that the contributions of both phen and bpy to the QS values are nearly the same, with phen expected to give a QS larger by only 0.04 mm/s in a tin molecule containing alkyl groups.[50] While some of the substituted ligands would be expected to present steric inhibition to the *trans*-$(CH_3)_2Sn$ O_h geometry apparently adopted by the unsubstituted parent compounds, there is no evidence for this in the QS data tabulated in Table II. Likewise, no systematic variation of IS value with substituent effect is seen. A similar constancy of IS value has recently been noted in substituted aryltrimethyltin compounds.[51]

Infrared Data. Far-infrared bands appearing below 600 cm^{-1} are shown in Table III, while bands between 1700 and 600 cm^{-1} are listed in Table IV.[52]

Phenanthroline band assignments have been made on the basis of comparisons with the spectra of benzene derivatives,[53] and the major bands assigned as follows: 1618 cm^{-1}, aryl C=N vibration;[54] 1589, 1560, 1503, 1420 cm^{-1}, aryl C=C and ring vibrations; 1250–1125 cm^{-1}, in-plane δ(C–H) deformations and ring vibrations; 850 cm^{-1}, out-of-plane δ(C–H) on the heterocyclic rings; 409 cm^{-1}, a ring deformation.[55]

A normal-coordinate analysis is available for bipyridine,[56] which exists in the trans-coplanar configuration in the solid state and whose spectrum is similar to but less complex than that of phen. The phenyl ring stretching modes have been assigned at 1579, 1553, 1448, 1410, and 1248 cm^{-1}, in-plane δ(C–H) at 1210, 1138, 1090, and 1083 cm^{-1}, out-of-plane δ(C–H) at 1039, 890, 753, and 738 cm^{-1}, and ring bending and torsion modes at 710, 651, 618, and 398 cm^{-1}. The out-of-plane δ(C–H) patterns arise in phenanthroline from one group of two and two groups of three adjacent hydrogens to give two separate absorptions, while in bipyridine there are two identical groups of four adjacent hydrogen atoms each to give rise to a single δ(CH) out-of-plane deformation mode. The multiple splittings which these bands exhibit in most of the spectra tabulated in Tables III and IV probably arise from out-of-plane hydrogen motions other than the one in which all of the atoms move in phase and also possibly from overtones of low-lying fundamentals in resonance.

There are no literature reports on the infrared spectra of substituted phenanthrolines. The group of three medium bands in the 1620–1500-cm^{-1} range remains relatively unaffected by substitution, although only two of these bands appear in the 5,6-dimethyl and tetramethyl derivatives. The band at 409 cm^{-1} is absent in derivatives substituted in the 4,7 positions (see Table III). Bands arising from phenyl substituents overlap those of the ligand ring vibrations. Major bands arising from other functional groups may be reasonably assigned as follows:[57] methyl, medium-intensity bands at 1390–1380 and 1490–1450 cm^{-1} (the latter for all except the tetramethyl derivative); nitro, strong bands at 1560 and 1345 cm^{-1}; halo, no absorptions in the regions expected for the aryl–Cl (1100–1030 cm^{-1}) or aryl–Br (1070–1030 cm^{-1}) stretches but strong bands lying at 934 cm^{-1} in the 5-Cl and at 914 cm^{-1} in the 5-Br spectra; another strong band at 910 cm^{-1} in the 5-Cl derivative may also be associated with the ν(aryl–Cl) mode. The strong bands at 873 and 867 cm^{-1} in the 5-Br derivative are probably associated with out-of-plane δ(C–H) deformation modes, however (see Table IV).

Several variously substituted bipyridyls have been studied in the infrared spectra.[58] The 4,4'-Me$_2$bpy ligand used in this study differs from the unsubstituted bpy in the 2000–1650-cm^{-1} region in which the overtone and combination bands of the δ(C–H) out-of-plane deformation as well as summation bands arising from ring deformation fundamentals lie. The band near 1370 cm^{-1} arising partly from the alkyl group δ(C–H) mode has also been shown to be characteristic of all 4,4'-disubstituted derivatives and may be associated with an in-plane ring stretching mode or with an overtone of an out-of-plane ring deformation near 700 cm^{-1}. The ring breathing mode[55] at 991 for bpy[56] is found at 992 cm^{-1} for the 4,4'-dimethyl derivative (see Table IV).

Uncomplexed dimethyltin dichloride shows ν_{asym}(Sn–C) at 560 cm^{-1} and ν_{sym}(Sn–C) at 524 cm^{-1} with ν(Sn–Cl) at 361 cm^{-1}.[8] On complexation with phen or bpy derivatives only a single ν(Sn–C) absorption is observed, lying in the region of the asymmetric stretch (see Table III). This evidence corroborates the *trans*-(CH$_3$)$_2$Sn assignment drawn from the Mössbauer QS value of ca. 4 mm/s, since in such a stereochemical situation the ν_{sym}(Sn–C) mode would be expected to be infrared inactive. The tin–chlorine stretching frequency is, on the other hand, lowered by ca. 100 cm^{-1} on complexation with phen or bpy.[8] Unfortunately, the tin–chlorine bands listed in Table III were too broad to resolve the hoped for ν_{asym}- and ν_{sym}(Sn–Cl) stretches which would have allowed stereochemical information to be derived. However, the Cl$_2$Sn moiety must in a cis configuration, once it is known that the (CH$_3$)$_2$Sn group is trans.

Normal-coordinate analysis has been carried out on 1:1 transition metal complexes of bpy.[59] Like these, in our systems the ligand bands are generally raised to higher frequency on coordination. For example, the out-of-plane ring deformations at 409 and 398 cm^{-1} in the free phen and bpy listed in Table III are raised to 419 and 427 cm^{-1}, respectively, in the spectra of the complexes.[8] The ligand bands associated with the in-ring C=C and C=N stretches shift to higher frequencies on complexation indicating that formation of the nitrogen to tin bonds is accompanied by an increase in the force constants of the bonds in the aromatic system of the ligands.

Of considerable interest would be the frequency of the tin–nitrogen coordinate bond stretch in our complexes. The weak band appearing at ca. 350 cm^{-1} in the bpy adducts of R$_2$SnCl$_2$ compounds which is present in the spectra of neither the free organotin chloride nor the ligand has been assigned to ν(Sn←N),[6] but this suggestion has been criticized.[8,60] The assignment of transition metal–nitrogen stretching frequencies in phen and bpy complexes[61,62] has also been criticized.[59,63] The assumption that new bands arising on complex formation are the metal–nitrogen stretching modes is not necessarily valid since a ligand vibration inactive in the free ligand may be activated in the adduct, and changes in the spectrum of bpy on complex formation may be associated with its change from the transoid to the cisoid configuration. Unequivocal metal–ligand band assignments must await metal[63] or nitrogen[64] isotopic substitution.

Formation Constants and Thermodynamic Values. Spectroscopic methods have been used to determine formation constants for tin(IV) chloride and organotin chloride adducts with bpy in acetonitrile,[7,10,17] and a log K of 3.30 ± 0.02 at 25 °C for the enthalpy of formation of (CH$_3$)$_2$SnCl$_2$·bpy has been reported.[10] The formation constants of dimethyltin dichloride adducts with phen[4] and three substituted-phen ligands[13] have also been measured in aqueous solution, with the order of log K values as 5-CH$_3$ > H > 5-Cl > 5-NO$_2$,[13] and calorimetry in benzene gave K in l./mol, $\Delta G°$ and $\Delta H°$ in kJ/mol, and $\Delta S°$ in J/(deg mol) as 123, −12.1, −64.8, and −174 for bpy and 5 × 10^4, −27, −86.0, and −195 for phen for M concentrations of 0.5 to 2.2 M.[65]

The changes in the spectrum of unsubstituted phen (1.5 × 10^{-5} M in acetonitrile) with the addition of dimethyltin dichloride (M) in various concentrations are shown in Figure 1. At ratios of M to ligand (L) of <10^3:1, an isosbestic point is observed at 264 nm, indicating the formation of a single adduct species, presumably (CH$_3$)$_2$SnCl$_2$·phen. At higher M:L concentration ratios, however, the absorbance pattern changes again. This behavior is more striking in the spectrum of 4,7-(CH$_3$)$_2$phen which is shown in Figure 2. Figure 2a shows the spectra for low M:L ratios at which an isosbestic point is observed at 264 nm, indicating the formation of the 1:1 complex. The spectra produced by this complex remain constant to ratios of <10^3:1, but at higher ratios (Figure 2b) a second isosbestic point indicates the formation of a new complex.

Because of the extremely high M:L ratios involved, the second complex could not be isolated, but it seems probable that equilibria of the following type are involved

$$(\mathrm{CH_3})_2\mathrm{SnCl_2} + (\mathrm{CH_3})_2\mathrm{SnCl_2}\cdot\mathrm{phen} \rightleftharpoons [(\mathrm{CH_3})_2\mathrm{Sn}\cdot\mathrm{phen}]^{2+} + [(\mathrm{CH_3})_2\mathrm{SnCl_4}]^{2-} \qquad (5)$$

in which the properties of the product dication in aqueous solution have been discussed,[4] and the dianion has been isolated

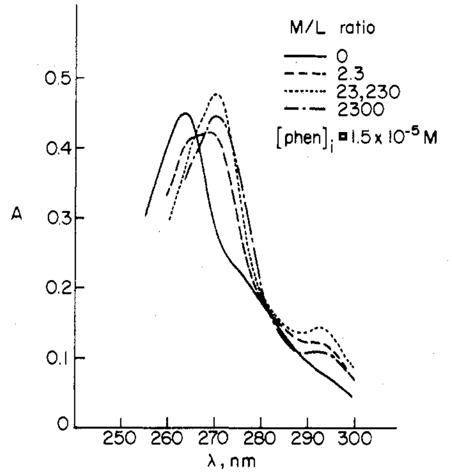


Figure 1. Spectra of phenanthroline (L) in acetonitrile with the addition of dimethyltin dichloride (M) at various M:L ratios.

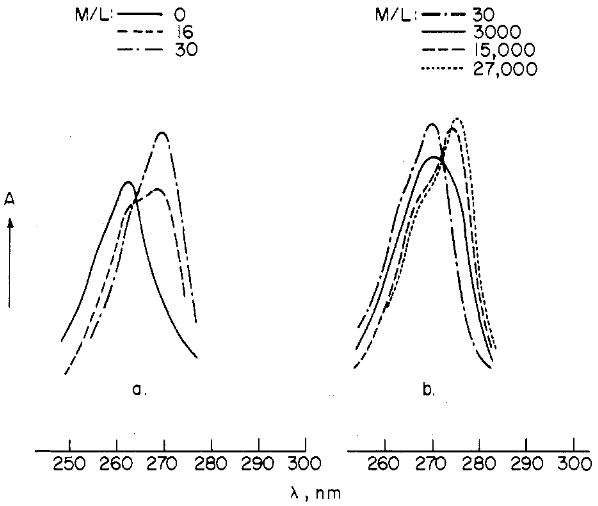


Figure 2. Spectra of 4,7-dimethylphenanthroline (L) in acetonitrile with the addition of dimethyltin dichloride (M) at low (a) and high (b) M:L ratios.

as the tetramethylammonium and cesium salts.[9] It is also possible to write

$$2(CH_3)_2SnCl_2 + (CH_3)_2SnCl_2\cdot phen \rightleftarrows [(CH_3)_2Sn\cdot 2phen]^{2+} + 2[(CH_3)_2SnCl_3]^- \quad (6)$$

in which the dianion has been isolated as the tetraethylammonium salt,[66] and an x-ray structure is available.[67] The six-coordinated dication finds its precedent in the tetrapyridine adduct of silicon tetraiodide[68] which is formulated as *cis*-$[SiI_2\cdot 4py]^{2+}(I^-)_2$. The four-coordinated cation depicted in eq 5 would be expected to be further solvated by acetonitrile to achieve higher coordination at tin. All of the phen ligands studied exhibited the second isosbestic point with excess dimethyltin dichloride, but it was most pronounced for those ligands which gave the highest first formation constants. An additional alternative would involve the bidentate phen ligand in a molecular as opposed to ionic, nonchelated structure with five-coordinated tin

$$(CH_3)_2SnCl_2 + (CH_3)_2SnCl_2\cdot phen \rightleftarrows [(CH_3)_2SnCl_2]_2\cdot phen \quad (7)$$

Changes in isosbestic points at high M:L ratios in acetonitrile have been seen in the $SnCl_4\cdot$bpy system,[7] and 2:1 complexes of organotin isocyanates[69] and isothiocyanates[70] have been isolated and interpreted[71] according to eq 7, but bpy, unlike phen, can adopt a transoid configuration, and we favor the ionic or ion-pair formulations in eq 5 and 6.

Table V. Stability Constants for the Species 5-RLH$^+$ and $(5\text{-RL})_3M^{2+}$ where L = phen and M = Fe^{2+} and Cu^{2+}

R	Water[a]	Water-dioxane[b]	Fe^{2+}-water[a]	Cu^{2+}-dioxane[b]
CH_3	5.23	4.65	22.3	4.60
H	4.96	4.53	21.3	4.50
C_6H_5	4.80	4.03	21.1	4.05
Cl	4.26	3.43	19.7	3.72
NO_2	3.57	2.80	17.8	3.25

[a] Reference 72. [b] Reference 73.

Table VI. Equilibrium Constants and Thermodynamic Data for $(CH_3)_2SnCl_2$ Adducts of 5-Substituted Phenanthrolines and 4,4'-Disubstituted Bipyridyls, L, at 298 K in Acetonitrile

L	K_{eq}	log K	ΔG[a]	ΔH[a]	ΔS[b]
5-CH_3phen	1.21 x 10^6	6.30	−8.29	−16.6	−27.8
phen	4.84 x 10^5	5.68	−7.75	−12.4	−15.7
5-C_6H_5phen	5.31 x 10^5	5.73	−7.81	−15.7	−26.4
5-Cl(phen)	8.22 x 10^4	4.91	−6.70	−14.1	−24.8
5-Br(phen)	6.2 x 10^4	4.79	−6.54	−13.1	−21.9
5-NO_2phen	1.9 x 10^4	4.28	−5.81	−11.6	−19
bpy	2.6 x 10^3	3.42	−4.67	−12.3	−25.7
4,4'-$(CH_3)_2$bipy	9.46 x 10^3	3.98	−5.42	−11.3	−19.7

[a] In kcal/mol. [b] In eu.

bpy and phen are weak bases, forming monoprotonated species. Typical values for the stability constants (i.e., pK_a's) of the monoprotonated bpy and phen species in water[72] and 50% dioxane–water mixtures[73] are shown in Table V. It is seen that the order of the phen ionization constants is 5-CH_3 > H > 5-C_6H_5 > 5-Cl > 5-NO_2 and that this same order is followed in the stability constants of the tris(5-substituted phenanthroline)iron(II)[72] and -copper(II)[73] complexes in water and 50% dioxane–water, respectively.[74] However, comparisons between pK_a values for the ionization of monosubstituted phenanthrolinium ions and the log K values for complex formation of the corresponding phenanthrolines are generally not justified, since in the formation of complexes both nitrogen atoms are involved in bonding to the central metal atom, and no question of tautomerism in the organic ligand arises. Discrepancies between observed and calculated values for certain 5-substituted phen's have been interpreted in terms of protonation on coordinated water molecules rather than on the phen nitrogen atoms.[75] Despite these considerations, linear plots of log K_a vs. the log of the dissociation constants are usually obtained, indicating the general dependence of complexing ability on the base strengths of the ligands.[72,73,76,77] bpy is a weaker base by far than phen toward the proton in aqueous media, but the 4,4'-dimethyl derivative is a good deal stronger.[67]

The formation constants listed in Table VI for dimethyltin dichloride adducts with the 5-substituted phen and 4,4'-disubstituted bpy derivatives also follow roughly the trend of the pK_a values of the monoprotonated organic bases in aqueous media, as do the tris divalent transition metal ion complexes. Only the log K values of the phen and 5-C_6H_5phen derivatives seem reversed in the organotin chloride adducts, but as with the divalent iron complexes in water, the formation constants of these two ligands are very close, probably within experimental error. The phenyl group is expected to be more electron withdrawing than hydrogen in this situation, but, unfortunately, no other formation constants of complexes of 5-C_6H_5phen than those shown in Table V are available in the literature. Without more data it is impossible to determine whether the apparent deviation from anticipated behavior shown in the sequence in Table VI is significant. Barring this result for the phenyl derivative, the other data for the phen ligands in Table VI agree in their sequence with equilibrium measurements of substituted phen adducts with $(C_2H_5)_2Sn^{2+}$,

$(CH_2{=}CH)_2Sn^{2+}$, and $(ClCH_2)_2Sn^{2+}$ cations in an aqueous acetate ion medium where the order was also found to be 5-CH_3 > H > 5-Cl > 5-NO_2.[13]

The K_{eq} values for the bpy and 4,4'-$(CH_3)_2$bpy ligands are in both cases smaller than those of the phen ligands. In 50% dioxane–water the pK_a values for bpy and 4,4'-$(CH_3)_2$bpy are 3.62 and 4.40, respectively, similar to those for the 5-Cl and unsubstituted phen, respectively, in that medium, while in pure water the pK values for phen, bpy and the 4,4' derivative are 4.97, 4.50, and 5.45, respectively.[73]

Several studies have been carried out on the bpy adducts of tin chlorides in acetonitrile,[7,10,17] and the formation constant has been measured as log $K = 3.30 \pm 0.02$ at 25 °C for $(CH_3)_2SnCl_2$·bpy,[10] a value close to that we list in Table VI.

Acetonitrile is of course itself a coordinating solvent toward tin compounds, and a stable 1:2 adduct of tin(IV) chloride has been isolated[78] whose stepwise formation constants have been reported as $K_1 = 12.8$ and $K_2 = 1.65$.[10] For $SnCl_4$ the formation of the bpy adduct then involves a ligand-exchange equilibrium

$$SnCl_4 \cdot 2CH_3CN + bpy \rightleftarrows SnCl_4 \cdot bpy + 2CH_3CN \qquad (8)$$

However, substitution of methyl for chlorine reduces the Lewis acidity and the solvation by acetonitrile drastically. The heat of mixing of CCl_4 solutions of tin chlorides with acetonitrile at 25 °C falls from 33.44 for $SnCl_4$ to 5.37 kcal/mol for $(CH_3)_2SnCl_2$.[10] The special nature of the $SnCl_4$ example is further shown by the positive entropy change in the formation of its bpy adduct by the ligand-exchange reaction; three molecules are formed from two as shown in eq 8, which counterbalances the loss of translational and rotational freedom by the bpy molecule on forming the chelate complex. In the dialkyltin dichloride series it has been shown that stronger solvation of acetonitrile increases the entropy change in complex formation where the order is $CH_3 > C_2H_5 > n\text{-}C_3H_7 \simeq n\text{-}C_4H_9$. In comparison with tin(IV) chloride, Okawara et al. found the relative order toward bpy to be $SnCl_4$ (3.3×10^3) > $(CH_3)_2SnCl_2$ (1.5) in acetonitrile.[10]

All of the entropy values listed in Table VI are negative, signifying that the release of two solvent molecules in the ligand-exchange equilibrium in eq 8 does not predominate. In the 5-substituted phen series the most negative entropy values are roughly associated with the most negative enthalpy values as with the 5-CH_3 derivative which possesses at once the most negative ΔS and ΔH values. Thus the formation of the adduct of the 5-CH_3 derivative is as expected the most exothermic, but this process is productive of the most order in the system as well. The 5-NO_2 derivative forms its tin adduct in the least exothermic reaction among the substituted phen ligands, as expected. Unlike the case in the phen series, the unsubstituted bpy gives rise to a greater entropy change than the 4,4'-dimethyl derivative. The simple phen ligand exhibits an enthalpy change which places it between the 5-Br and 5-NO_2 derivatives, but adduct formation is accompanied by the smallest negative entropy of any of the ligands studied, and the resulting equilibrium constant lies between those of the 5-alkyl and 5-aryl derivatives. Because of the significant differences among the entropy values in Table VI, the relative order of K_{eq} and ΔG values will depend upon the temperature chosen.

NMR Data. In Table VII we list $|J(^{119}Sn\text{–}C\text{–}^1H)|$ values for the 5-substituted-phen adducts studied. Unfortunately, the bpy complexes were too insoluble for NMR measurements, and dissociation of the soluble phen complexes in the methylene chloride is possible. The tin–proton coupling constant of dimethyltin dichloride in inert media such as methylene chloride is 70.0[79] and is given as 83.4 Hz in acetonitrile.[80] The magnitude of J rises to 121.1 in HMPA among an order which includes dioxane (73.5) < acetone (91.5) < DME (96.4) < DMF (109.8) < DMSO (114.8 Hz).[79] The values listed in Table VII are close to those of the recently reported substituted-picolinaldamine adducts of dimethyltin dichloride which are structurally similar to those of bpy and whose coupling constants range from 111.5 to 114.6 Hz.[80] Comparison of the J values in Table VII with the thermodynamic data in Table VI shows that the order of enthalpies, 5-CH_3 > 5-C_6H_5 > 5-Cl > 5-Br > H > 5-NO_2, is followed by the J values except for the parent ligand which returns to the top of the list, above the 5-CH_3 derivative.

Table VII. NMR Tin–Proton Coupling Constant Data for $(CH_3)_2SnCl_2 \cdot n$L (±0.2 Hz) in CH_2Cl_2

L	$\lvert J(^{119}Sn\text{–}C\text{–}^1H)\rvert$, Hz	L	$\lvert J(^{119}Sn\text{–}C\text{–}^1H)\rvert$, Hz
(CH_2Cl_2)	70.0[a]	5-Cl(phen)	113.5
$CH_3C{\equiv}N$	83.4[b]	5-C_6H_5phen	114.6
H_2O	101.9[c]	5-CH_3phen	114.9
5-NO_2phen	110.8	phen	115.6
5-Br(phen)	113.0		

[a] From ref 79. [b] From ref 80. [c] From ref 84.

In their study of trimethyltin chloride adducts, Drago et al. found that the enthalpies of formation were in fact linearly related to the tin–proton coupling constants, and the extrapolation of the line drawn through the experimental points yielded the $J(^{119}Sn\text{-}C\text{–}^1H)$ value measured for free trimethyltin chloride at $\Delta H° = 0$. The plot was used to obtain enthalpies of systems of donors too weak to measure directly.[81]

The plot of $|J(^{119}Sn\text{–}C\text{–}^1H)|$ vs. $\Delta H°$ for our six phen adducts when the value for dimethyltin dichloride in acetonitrile is included as a data point at $\Delta H° = 0$ gives a line of slope −2.01, whose intercept is 85.4 Hz with a correlation coefficient of 0.963. However, all but one data point are gathered into too narrow a range to lend confidence in this treatment.

Finally, the question of adventitious moisture in the acetonitrile solvent system employed in these studies must be addressed. Wardell[82] has criticized the accuracy of the very large (ca. 5×10^6) equilibrium constant obtained for the tin(IV) chloride–bipyridine formation by Okawara et al.[7] on the basis of the low ligand (10^{-5} M) and tin(IV) chloride concentrations (10^{-6}–10^{-2} M) in the spectroscopic method employed. At the lower molarities of the halide, water would have been present in comparable concentrations to give significant hydrolysis. In the present study a much weaker Lewis acid than tin(IV) chloride was employed. To check the effect of solvent moisture on the thermodynamic values listed in Table VI we redetermined certain values in undried, reagent grade acetonitrile labeled as containing <0.05% water.[83] The K_{eq}, $\Delta G°$ (kcal/mol), $\Delta H°$ (kcal/mol), and $\Delta S°$ (eu) values were found to be as follows, respectively: phen, 6.0×10^4, −6.51, −6.51, 0; 5-NO_2phen, 5.1×10^3, −5.05, −7.97, −9.8; bpy, 21×10^3, −4.52, −11.7, −24; 4,4'-$(CH_3)_2$bpy, 5.3×10^3, −5.07, −9.45, −15. The differences between the values in wet solvent and those listed in Table V are greater for the highest equilibrium constant (phen) since smaller concentrations of dimethyltin dichloride could be used to measure these thermodynamic values. The zero entropy value received for the measurement of the adduct with phen would seem to indicate that at the low concentration of dimethyltin dichloride employed ($(2\text{–}3) \times 10^{-5}$ M) the reaction with water was extensive and that the release of water molecules from the diaquo complex in a ligand-exchange process such as that depicted in eq 8 became important. The entropy changes for all of the adducts measured in the wet solvent were lower, with that for bpy whose equilibrium constant is lowest and entropy change highest agreeing most closely with that listed in Table V. The equilibrium and thermodynamic values for the $(CH)_2SnCl_2$·bpy adduct in acetonitrile (2×10^3, −4.50, −11.8, −24.8) reported by Okawara et al.[10] most closely resemble those measured in the undried solvent system. As a further test of our system we extrapolated the line drawn through the points for the substituted-phen derivatives so that it intercepted $\Delta H^\circ = 0$ at a point which would represent the dimethyltin dichloride–aquo complex whose coupling constant has been measured at above 100 Hz.[84] The correlation coefficient for this plot was only 0.553, however.

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Registry No. $(CH_3)_2SnCl_2$·phen, 20742-26-1; $(CH_3)_2SnCl_2$·5-CH_3phen, 58384-16-0; $(CH_3)_2SnCl_2$·5,6-$(CH_3)_2$phen, 58384-17-1; $(CH_3)_2SnCl_2$·4,7-$(CH_3)_2$phen, 58384-18-2; $(CH_3)_2SnCl_2$·3,4,7,8-$(CH_3)_4$phen, 58384-19-3; $(CH_3)_2SnCl_2$·5-C_6H_5phen, 58384-20-6; $(CH_3)_2SnCl_2$·4,7-$(C_6H_5)_2$phen, 58384-21-7; $(CH_3)_2SnCl_2$·5-Clphen, 58384-22-8; $(CH_3)_2SnCl_2$·5-Brphen, 58384-23-9; $(CH_3)_2SnCl_2$·5-NO_2phen, 58384-24-0; $(CH_3)_2SnCl_2$·bpy, 12089-50-8; $(CH_3)_2SnCl_2$·4,4′-$(CH_3)_2$-bpy, 58384-25-1.

Supplementary Material Available: Table IV, listing ir bands between 1700 and 600 cm^{-1} for the ligands and their complexes (6 pages). Ordering information is given on any current masthead page.

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