

SPECTROPHOTOMETRIC STUDIES OF COMPLEX FORMATION. EQUILIBRIA OF SOME ORGANOTIN CHLORIDES AND TIN TETRACHLORIDE WITH 2,2'-BIPYRIDINE IN SOLUTION

MICHIHIRO KOMURA, YOSHIKANE KAWASAKI, TOSHIO TANAKA AND ROKURO OKAWARA

Department of Applied Chemistry, Osaka University, Higashinoda, Miyakojima, Osaka (Japan)

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INTRODUCTION

Recently, organotin chelate complexes, containing 8-hydroxyquinoline^{1,4,5}, 2,2'-bipyridine^{1,2,3,5}, 1,10-phenanthroline^{2,3,5}, and acetylacetone⁶ as chelating agents have been studied in many laboratories. The most complete investigation has employed 2,2'-bipyridine, which reacts readily with dialkyltin dichlorides or tin tetrachloride forming 1:1 complexes. The bipyridine complexes were all sparingly soluble in common solvents (ether, benzene or alcohol) suggesting polymeric association. The di-*n*-butyltin-bipyridine complex appears to dissociate somewhat in chloroform⁵.

Complex formation equilibria between 2,2'-bipyridine and tin compounds in solution has not been studied. We now wish to report some spectroscopic studies of complex formation equilibria between 2,2'-bipyridine and dimethyltin dichloride, di-*n*-butyltin dichloride or tin tetrachloride.

The spectra of solutions of bipyridine with the varying amounts of tin compounds were studied in acetonitrile, and stability constants were determined. The stability constant for $(C_4H_9)_2SnCl_2 \cdot bipy$ was also determined in some alcohols and esters to obtain information about the effect of solvents.

EXPERIMENTAL

Materials

2,2'-Bipyridine was special grade, m.p. 70-72°. Dimethyl- and di-*n*-butyltin dichloride were supplied by Nitto Kasei Co. Ltd., and purified by sublimation or recrystallization. All the dihalides were identified by their melting points. Tin tetrachloride was purified by distillation, b.p. 112-114°. Organic solvents were all purified according to procedures cited in the literature⁷.

Measurements of ultraviolet spectra

The ultraviolet spectra were measured on a Hitachi EPU-2A Spectrophotometer with 1 cm quartz cells. Ambient temperature, 17 ± 2° prevailed.

Determination of the stability constants

The K values were determined using the following equation:

$$\frac{1 - (D_0/D)}{[A]_0} = -K + K(\epsilon_{AB}/\epsilon_B)(D_0/D)$$

where ϵ_B and ϵ_{AB} are the molar extinction coefficients of 2,2'-bipyridine and its complex respectively. D_0 and D are the absorbances of a solution containing only 2,2'-bipyridine and of a series of solutions containing a constant amount of bipyridine but varying amounts of chloride. $[A]_0$ is the total concentration of the chloride.

RESULTS AND DISCUSSION

It is well known that the strong electron acceptor power of tin tetrachloride is greatly decreased by alkyl substitution. We find that the stability constant for $\text{SnCl}_4 \cdot \text{bipy}$ (Table 1) is about one thousand times larger than that for $(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{bipy}$. However, there is little difference in the equilibrium constants for $(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{bipy}$ and $(\text{C}_4\text{H}_9)_2\text{SnCl}_2 \cdot \text{bipy}$. It has been reported that in the infrared spectra of tin

TABLE 1

THE STABILITY CONSTANTS FOR THE COMPLEXES FORMED BY VARIOUS TIN CHLORIDES WITH 2,2'-BIPYRIDINE IN ACETONITRILE

Complexes	$\log K$
$(\text{C}_4\text{H}_9)_2\text{SnCl}_2 \cdot \text{bipy}$	3.19 ± 0.03
$(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{bipy}$	3.36 ± 0.04
$\text{SnCl}_4 \cdot \text{bipy}$	6.7 ± 0.3

acetylacetonates⁸ or oxinates of the type R_2SnL_2 ($\text{L} = \text{acac}$ or oxine), the Sn-O stretching vibration goes to lower wave number as R changes in the order: $\text{Cl} > \text{Br} > \text{I} > \text{C}_6\text{H}_5 > \text{CH}_3 > \text{C}_2\text{H}_5 \approx n\text{-C}_3\text{H}_7 \approx n\text{-C}_4\text{H}_9$. Thus electron-attracting groups attached to tin apparently decrease the electron density on the central tin atom and strengthen the bond to the coordinating group.

The $\log K$ values for $(\text{C}_4\text{H}_9)_2\text{SnCl}_2 \cdot \text{bipy}$ shown in Table 2 clearly increase with increasing polarity of the solvent. Thus it might be suggested that the Sn-Cl bond is affected by the coordination of bipyridine to tin; $\text{N}^{\delta+} \rightarrow \text{Sn}-\text{Cl}^{\delta-}$, the stability of which would depend on the polarity of the solvent.

The $\log K$ values in ethanol and diethyl malonate are about the same (Table 2). This observation is probably due to some difference of solvation between these solvents.

Figures 1 and 2 show the ultraviolet spectrum of 2,2'-bipyridine in the presence of varying amounts of dimethyltin dichloride and tin tetrachloride, respectively. 2,2'-Bipyridine seems to form only a 1:1 complex with dimethyltin dichloride, but two types of complexes apparently form with tin tetrachloride. At low concentrations of SnCl_4 , a 1:1 complex is found with a spectrum similar to that of the $(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{bipy}$ complex. The absorption maxima for these complexes appear near $300 \text{ m}\mu$,

TABLE 2

THE STABILITY CONSTANTS FOR $(C_4H_9)_2SnCl_2 \cdot bipy$ IN VARIOUS SOLVENTS

Solvents	Dielectric constants ²	log K
<i>Alcohols</i>		
Methanol	32.6	3.41 \pm 0.02
Ethanol	24.3	2.31 \pm 0.01
<i>n</i> -Propanol	20.1	2.28 \pm 0.01
<i>n</i> -Butanol	17.1	2.11 \pm 0.01
<i>Esters</i>		
Diethyl malonate	7.9	2.45 \pm 0.03
Methyl acetate	6.7	2.10 \pm 0.03
Butyl acetate	5.0	1.76 \pm 0.06

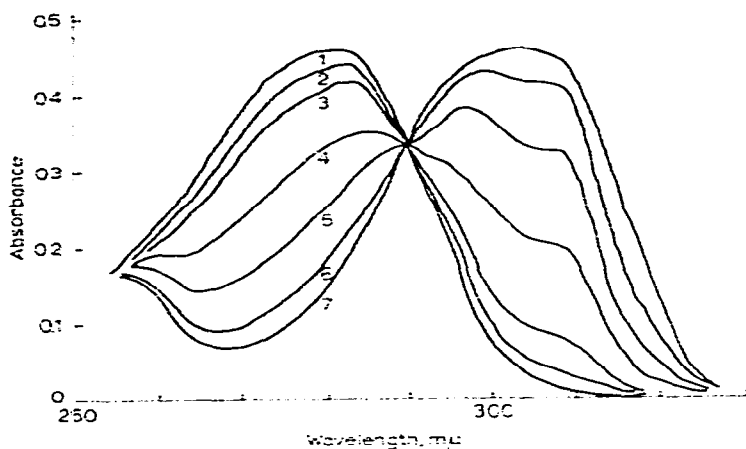


Fig. 1. The absorption spectra of 2,2'-bipyridine in acetonitrile (3×10^{-5} mol/l), containing varying amounts of dimethyltin dichloride: (1) 0, (2) 3×10^{-5} , (3) 9×10^{-5} , (4) 3×10^{-4} , (5) 9×10^{-4} , (6) 3×10^{-3} , (7) 9×10^{-3} mol/l.

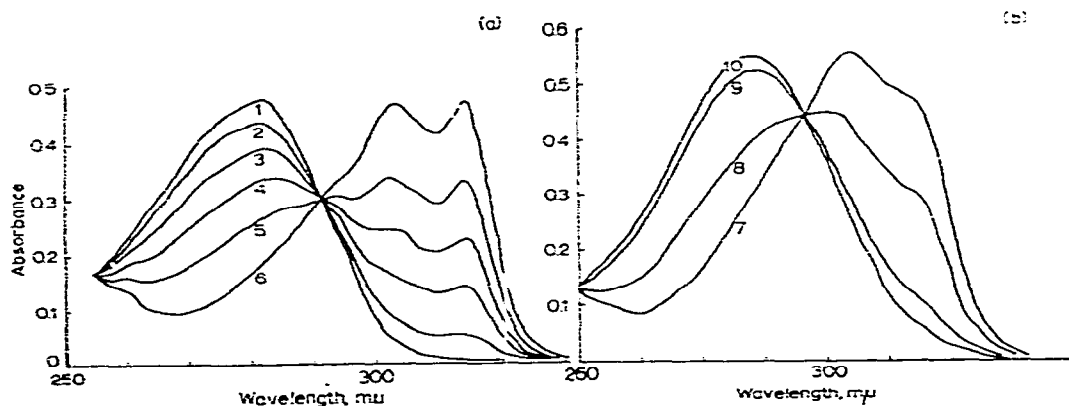


Fig. 2. The spectra of 2,2'-bipyridine in acetonitrile (3×10^{-5} mol/l), containing varying amounts of tin tetrachloride: (a); (1) 0, (2) 3×10^{-6} , (3) 9×10^{-6} , (4) 1.5×10^{-5} , (5) 2.1×10^{-5} , (6) 3×10^{-5} mol/l. (b); (7) 3×10^{-3} , (8) 9×10^{-3} , (9) 1.5×10^{-2} , (10) 3×10^{-2} mol/l.

where 2,2'-bipyridine chelates are known to absorb. Thus both of the 1:1 complexes can be assigned the chelate structure, (I). At very high SnCl_4 concentration, a new absorption band appears at $288 \text{ m}\mu$. This is probably due to 2:1 complexing with the bipyridine molecule in the bridging form (II)*.

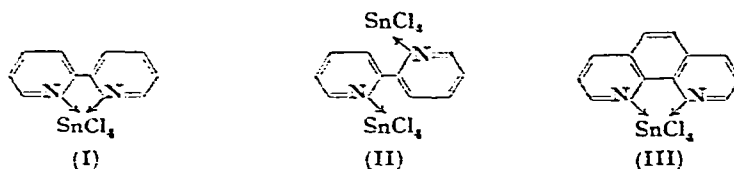


Figure 3 shows the spectrum of 1,10-phenanthroline with SnCl_4 ; these compounds are known to react to form a 1:1 complex¹⁰. Spectral evidence is found only for a 1:1 complex, with structure (III). 1,10-Phenanthroline is obviously incapable of forming a 2:1 complex analogous to (II).

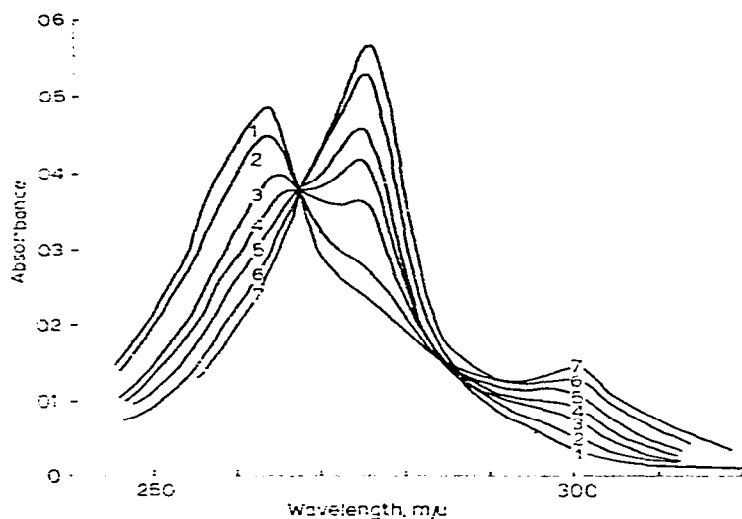


Fig. 3. The spectra of 1,10-phenanthroline- H_2O in acetonitrile ($1.5 \times 10^{-5} \text{ mol/l}$), containing varying amounts of tin tetrachloride: (1) 0, (2) 1.5×10^{-6} , (3) 4.5×10^{-6} , (4) 7.5×10^{-6} , (5) 1.05×10^{-5} , (6) 1.5×10^{-5} , (7) $1.5 \times 10^{-2} \text{ mol/l}$.

The position of the absorption maxima of bridging species (II) or chelating species (I) are almost the same as those of doubly protonated bipyridine and mono-protonated bipyridine, respectively, as reported by Nakamoto¹¹. These results are interesting, for they suggest that there may be little delocalization of ligand π -electrons to tin through $d_{\pi}-p_{\pi}$ bonding.

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* Diphenyltin diisocyanate complex containing bridging bipyridine group has been recently prepared⁹.

SUMMARY

The stability constants of 2,2'-bipyridine complexes of dimethyltin dichloride, di-*n*-butyltin dichloride and tin tetrachloride were measured spectroscopically, and the tin tetrachloride complex was found to be much more stable than the others. The stability constant for the dibutyltin dichloride complex increases with increasing solvent polarity. From the ultraviolet band maximum, the configuration of 2,2'-bipyridine in complexes formed in solution was determined. Only the chelating form was found for dialkyltin dichlorides, but for tin tetrachloride, the existence of both chelating and bridging forms was suggested.

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