

ORGANOMETAL COMPLEXES
I. DIORGANOTIN BIS(8-HYDROXYQUINOLINATES), DIORGANOTIN-
(2,2'-BIPYRIDYL) DICHLORIDES AND DIALKYL TIN-
(1,10-PHENANTHROLINE) DICHLORIDES

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Several stable complexes formed between diorganotin dihalides and bidentate ligands such as 8-hydroxyquinoline¹, 2,2'-bipyridyl and 1,10-phenanthroline² have already been characterized. These compounds are interesting in that they involve both organometallic chemistry and the chemistry of complexes; also there is the possibility that stereo- and optical isomers of these substances may exist.

This paper reports the preparation and properties of a series of complexes obtained by the reaction of dialkyl- and diphenyltin dichlorides with 8-hydroxyquinoline, 2,2'-bipyridyl and 1,10-phenanthroline. The configurations and the stability constants of some of these complexes are also described.

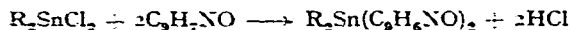
EXPERIMENTAL

Materials

Dimethyl-, diethyl-, di-*n*-propyl-, di-*n*-butyl- and diphenyltin dichlorides were supplied by Nitto Kasei Company, and purified by recrystallization or sublimation. 8-Hydroxyquinoline, 2,2'-bipyridyl and 1,10-phenanthroline monohydrate were used after purification of commercial materials by suitable methods.

Diorganotin bis(8-hydroxyquinolines)

An ethanol solution of dialkyl- or diphenyltin dichloride was mixed with 8-hydroxyquinoline in ethanol (mole ratio 1:2) and followed by neutralization with aqueous ammonia.



The fine yellow precipitates formed were recrystallized from benzene or ligroin. All of these bright yellow crystalline compounds are stable in air and have the composition $R_2Sn(C_9H_6NO)_2$. They are soluble in common organic solvents, but insoluble in water. Melting points and analytical data are shown in Table 1.

When the diorganotin dichlorides were reacted with 8-hydroxyquinoline at a mole ratio of 1:1 or 1:0.5 and then neutralized, mixtures of diorganotin bis(8-hydroxyquinolate) and diorganotin oxide were obtained, and no diorganotin chloride 8-hydroxyquinolate was formed.

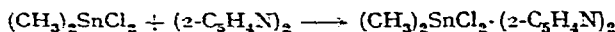
TABLE 1
MELTING POINTS AND ANALYTICAL DATA OF DIORGANOTIN
BIS(8-HYDROXYQUINOLINATES)

$R_2Sn(C_9H_6NO)_2$	<i>m.p.</i> (°C)	C (%) Found (Calcd.)	H (%) Found (Calcd.)	Sn (%) Found (Calcd.)
R = CH ₃	231-233	55.16 (54.92)	3.98 (4.12)	27.20 (27.16)
C ₂ H ₅	167-168	56.76 (56.77)	4.69 (4.73)	25.29 (25.53)
<i>n</i> -C ₃ H ₇	151-153	58.36 (58.42)	5.24 (5.27)	24.02 (24.08)
<i>n</i> -C ₄ H ₉	150-152 (154.5-155.5)*	59.63 (59.88)	5.73 (5.76)	22.53 (22.78)
C ₆ H ₅	251-252 (231-233)*	64.02 (64.21)	4.00 (3.92)	21.65 (21.17)

* Ref. 1.

Diorganotin(2,2'-bipyridyl) dichlorides

When ethereal solutions of dimethyltin dichloride and 2,2'-bipyridyl were mixed (mole ratio 1:1), a white precipitate appeared immediately.



The precipitate was purified by recrystallization from a large amount of benzene. Diethyl, di-*n*-propyl, di-*n*-butyl and diphenyl derivatives have similarly been synthesized from the corresponding diorganotin dichlorides. All of these complexes are also stable in air. They are generally soluble to some extent in polar solvents, less soluble in non-polar organic solvents, and the solubilities decrease with decreasing size of the alkyl groups. Melting points and analytical data are shown in Table 2.

TABLE 2
MELTING POINTS AND ANALYTICAL DATA OF DIORGANO-
TIN(2,2'-BIPYRIDYL) DICHLORIDES

$R_2SnCl_2 \cdot (2-C_5H_4N)_2$	<i>m.p.</i> (°C)	C (%) Found (Calcd.)	H (%) Found (Calcd.)
R = CH ₃	232-233	38.19 (38.12)	3.72 (3.73)
C ₂ H ₅	195-196 (200-201)*	41.87 (41.62)	4.46 (4.46)
<i>n</i> -C ₃ H ₇	204-205	44.19 (44.47)	5.26 (5.09)
<i>n</i> -C ₄ H ₉	177-179 (180)*	46.99 (46.97)	5.62 (5.65)
C ₆ H ₅	239-240 (243-245)*	52.74 (52.81)	3.48 (3.60)

* Ref. 2.

The amount of tin contained in these complexes was determined by the acid digestion method applicable generally to organotin compounds, but the observed values were always considerably smaller than the calculated ones. This may be due to the formation of some volatile substances during the sulfuric acid digestion.

Dialkyltin(1,10-phenanthroline) dichlorides

Dimethyltin and diethyltin derivatives were prepared and purified by a procedure quite similar to that used to obtain the diorganotin(2,2'-bipyridyl) dichlorides. These two derivatives are also similar to the dialkyltin(2,2'-bipyridyl) dichlorides with respect to appearance, stability in air, and solubility in various solvents. Melting points and analytical data are shown in Table 3.

TABLE 3
MELTING POINTS AND ANALYTICAL DATA OF DIALKYL-
TIN(1,10-PHENANTHROLINE) DICHLORIDES

$R_2SnCl_2 \cdot C_{12}H_8N_2$	<i>m.p.</i> ($^{\circ}C$)	<i>C</i> (%) <i>Found</i> (<i>Calcd.</i>)	<i>H</i> (%) <i>Found</i> (<i>Calcd.</i>)
R = CH_3	decomp. 200	41.17 (42.03)	3.46 (3.50)
C_2H_5	230-231 (235-236) [*]	44.28 (44.89)	4.29 (4.21)

* Ref. 2

Molecular weight determinations

The molecular weight of di-*n*-butyltin bis(8-hydroxyquinolate) was measured by the cryoscopic method in benzene. Found 522, 532 and 517 for 0.9, 2.2 and 3.6% (w/w) solutions, respectively. Calculated for $(C_4H_9)_2Sn(C_9H_8NO)_2$ 521. Because of the poor solubilities of the lower dialkyltin(2,2'-bipyridyl) dichlorides, the di-*n*-butyl derivative was studied in boiling chloroform solution. Found 252, 262, 265 and 259 for 0.14, 0.27, 0.56 and 0.80% (w/w) solutions, respectively. Calculated for $(C_4H_9)_2SnCl_2 \cdot (C_{10}H_8N_2)$ 461.

Infrared and ultraviolet spectra

The infrared spectra were measured in nujol mulls using Hitachi EPI-2G Grating and Koken D. S. 401 IR Spectrophotometers for the 15-25 μ and 20-35 μ regions, respectively. The ultraviolet spectra were measured using a Hitachi EPS-2 UV Spectrophotometer.

RESULTS AND DISCUSSION

The diphenyltin bis(8-hydroxyquinolate) obtained in this study exhibited a considerably higher melting point than that reported by Blake *et al.*¹. However, our complex was prepared from diphenyltin dichloride, whereas Blake employed the corresponding dibromide. Therefore, the difference in the melting points might be due to formation of different isomers in the two cases.

It has been shown by a cryoscopic method that di-*n*-butyltin bis(8-hydroxy-

quinolate) is monomeric in benzene. Other diorganotin bis(8-hydroxyquinolates) are, therefore, also considered to be monomeric in the same solvent. On the other hand, a molecular weight determination in boiling chloroform suggests that di-*n*-butyltin(2,2'-bipyridyl) dichloride dissociates to a considerable extent in this solvent.

The infrared spectrum of $(\text{CH}_3)_2\text{Sn}(\text{OX})_2$ [dimethyltin bis(8-hydroxyquinolate)] is shown in Fig. 1, together with those of 8-hydroxyquinoline and dimethyltin dichloride.

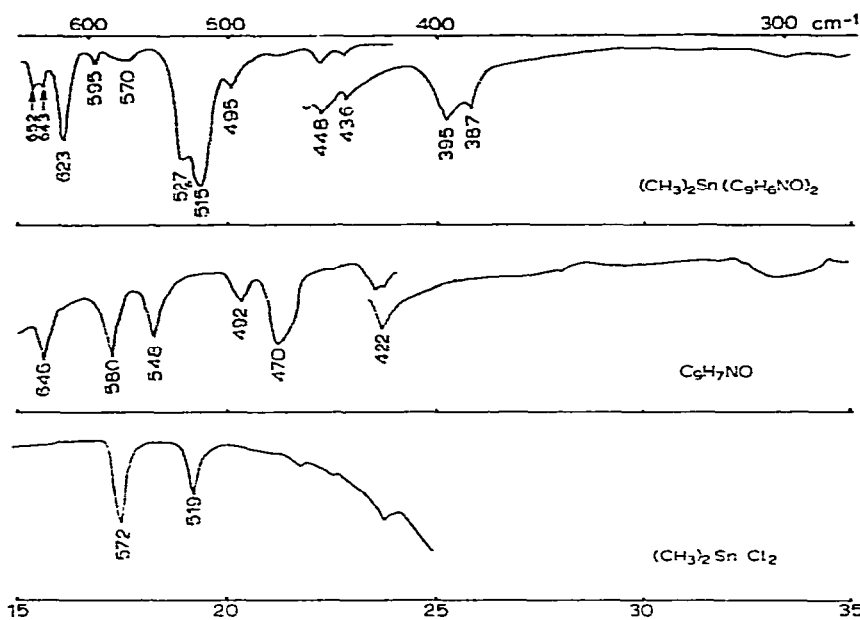


Fig. 1. Infrared spectra of $(\text{CH}_3)_2\text{Sn}(\text{OX})_2$, 8-hydroxyquinoline and dimethyltin dichloride

The absorption bands at 572 cm^{-1} and 519 cm^{-1} in the spectrum of $(\text{CH}_3)_2\text{SnCl}_2$ have been assigned to the asymmetric and symmetric stretch of the Sn-C bonds, respectively³. It can be seen in Fig. 1 that formation of the complex is accompanied by the appearance of two strong bands at 515 cm^{-1} and 395 cm^{-1} . These new absorption bands may, therefore, be associated with Sn-O and Sn-N stretch, respectively. The band at 527 cm^{-1} is tentatively assigned to Sn-C asymmetric stretch in $(\text{CH}_3)_2\text{Sn}(\text{OX})_2$. It is at present difficult to determine which band is associated with the Sn-C symmetric stretch in the complex, because there are also absorption bands associated with 8-hydroxyquinoline in the region of $450\text{--}500\text{ cm}^{-1}$. For this reason it is not clear which of the isomeric structures (see Fig. 2) is possessed by our $(\text{CH}_3)_2\text{Sn}(\text{OX})_2$; it may even be a mixture of isomers.

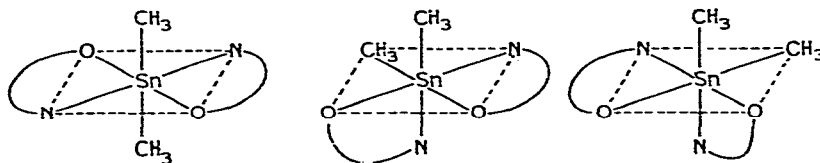


Fig. 2. Stereo and optical isomers of $(\text{CH}_3)_2\text{Sn}(\text{OX})_2$.
(Altogether there are six isomers including stereo and optical forms.)

The infrared spectra of $(\text{CH}_3)_2\text{SnCl}_2 \cdot (2\text{-C}_5\text{H}_4\text{N})_2$ and $(2\text{-C}_5\text{H}_4\text{N})_2$ (2,2'-bipyridyl) are shown in Fig. 3. There are two new bands at 427 cm^{-1} and 346 cm^{-1} in the spectrum of $(\text{CH}_3)_2\text{SnCl}_2 \cdot (2\text{-C}_5\text{H}_4\text{N})_2$. These bands seem to be associated with the asymmetric and symmetric stretch of Sn-N bonds, respectively. The band at 578 cm^{-1} in this complex can be assigned to the Sn-C asymmetric stretch, and the further weak band at 467 cm^{-1} might be associated with the Sn-C symmetric stretch, although the

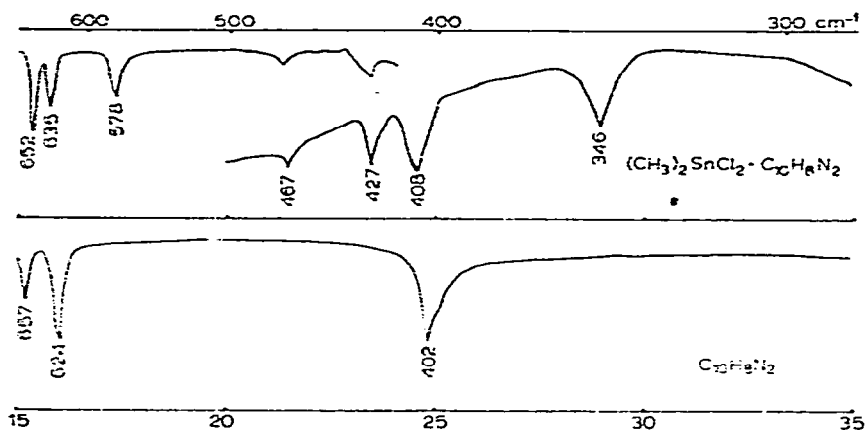


Fig. 3. Infrared spectra of $(\text{CH}_3)_2\text{SnCl}_2 \cdot (2\text{-C}_5\text{H}_4\text{N})_2$ and 2,2'-bipyridyl.

latter wave number is considered to be too low for the Sn-C symmetric mode. On the basis of these assignments, the $(\text{CH}_3)_2\text{SnCl}_2 \cdot (2\text{-C}_5\text{H}_4\text{N})_2$ obtained in the present experiment is considered to be one of the stereo- or optical isomers or their mixture, as shown in Fig. 4.

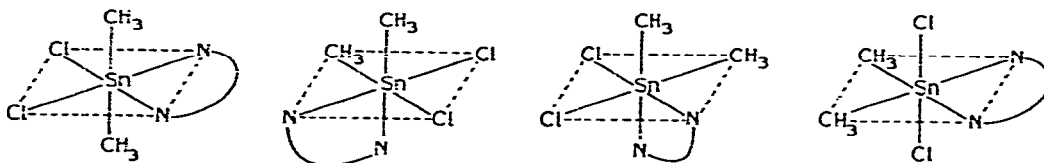


Fig. 4. Stereo- and optical isomers of $(\text{CH}_3)_2\text{SnCl}_2 \cdot (2\text{-C}_5\text{H}_4\text{N})_2$.

It was found by X-ray crystallographic analysis that the trimethyltin chloride-pyridine complex contains a five-coordinated tin atom⁴. Considering this fact, the existence of six-coordinated tin atoms in $(\text{CH}_3)_2\text{Sn}(\text{OX})_2$ and $(\text{CH}_3)_2\text{SnCl}_2 \cdot (2\text{-C}_5\text{H}_4\text{N})_2$ is reasonable.

The ultraviolet spectra of $(\text{CH}_3)_2\text{Sn}(\text{OX})_2$ and 8-hydroxyquinoline in ethanol were compared. The absorption peak at $318\text{ m}\mu$ in 8-hydroxyquinoline shifts to $372\text{ m}\mu$ upon formation of the complex. It has previously been found that this peak of 8-hydroxyquinoline is shifted generally to higher wave lengths, $370\text{--}430\text{ m}\mu$, in the transition-metal 8-hydroxyquinolinates, and the magnitudes of the shifts are parallel to the stability constants⁵. This tendency may suggest that the stability constant of $(\text{CH}_3)_2\text{Sn}(\text{OX})_2$ is comparable to that of transition-metal 8-hydroxyquinolinates.

Because of the poor solubilities of the lower dialkyltin(2,2'-bipyridyl) dichlorides, the ultraviolet spectrum of $(\mu\text{-C}_4\text{H}_9)_2\text{SnCl}_2 \cdot (2\text{-C}_5\text{H}_4\text{N})_2$ has been measured in ethanol,

cyclohexane and chloroform. The spectra of this complex in these solvents are quite similar to those of 2,2'-bipyridyl in the same solvents. From this fact and the result of the molecular weight determination, $(n\text{-C}_4\text{H}_9)_2\text{SnCl}_2 \cdot (2\text{-C}_5\text{H}_4\text{N})_2$ is considered to dissociate to a considerable extent in these solvents. In fact, when the solution contains di-*n*-butyltin dichloride in large excess relative to the amount of 2,2'-bipyridyl, a new absorption band associated with complex formation appears at a higher wave length, 300 $m\mu$. The stability constant of $(n\text{-C}_4\text{H}_9)_2\text{SnCl}_2 \cdot (2\text{-C}_5\text{H}_4\text{N})_2$ in ethanol has been obtained from the ultraviolet spectrum, and the result also shows that this complex dissociates to a fair extent in the solution. The details will be described in the following paper.

SUMMARY

By the reaction of dialkyl- and diphenyltin dichlorides with the bidentate ligands, 8-hydroxyquinoline, 2,2'-bipyridyl and 1,10-phenanthroline, a series of diorganotin complexes were prepared. From molecular weight determinations, and measurement of infrared and ultraviolet spectra of these complexes, the following results were obtained. (1) Diorganotin bis(8-hydroxyquinolinates) are monomeric in benzene solution and their stability possibly is comparable with that of transition-metal 8-hydroxyquinolinates. (2) Di-*n*-butyltin(2,2'-bipyridyl) dichloride dissociates to a considerable extent in solution. (3) All of these organotin complexes contain six-coordinated tin atoms.

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