

COMPLEXES OF ORGANOMETALLIC COMPOUNDS

V. DIPHENYLTIN(IV) AND TRIPHENYLTIN(IV) OXINATES

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We have been studying the complexes of organometallic cations with monodentate and bidentate ligands¹, and have recently completed some researches on ethyl- and phenylmercury oxinates in aqueous solution, and concluded that they are chelate complexes. These investigations were initiated to extend the knowledge of the coordination chemistry of organometallic compounds, and also possibly to employ *S*-quinolinol in their analytical chemistry. We now describe similar researches on the *S*-quinolinol complexes of diphenyltin(IV) and triphenyltin(IV) which were prepared in the solid state and then studied spectrophotometrically in ethanol solutions.

It was observed that the diphenyltin(IV) derivative, *i.e.* $(C_6H_5)_2Sn-(oxinate)_2$, is very probably a chelate complex, and that the triphenyltin(IV) derivative $(C_6H_5)_3Sn-(oxinate)$, is probably not a chelate complex. These findings noticeably extend the knowledge in this field. Previously only the compounds $R_2Sn-(oxinate)_2$ ($R = n$ -butyl and phenyl)² were known to exist in the solid state but these were not studied.

EXPERIMENTAL

Throughout this work reagents of high purity were used. The compounds $(C_6H_5)_2SnCl_2$ and $(C_6H_5)_3SnCl$ were supplied by Fluka A.G. and Eastman Kodak. Their melting points were used as a criterion of purity.

The preparation of the solid diphenyltin(IV) dioxinate was effected as shown in ref. 2. When the diphenyltin(IV) dichloride was used instead of the dibromide, as in ref. 2, no difference could be observed in the solid obtained. (Found: C, 63.7; H, 4.04; N, 4.93. $C_{30}H_{22}N_2O_2Sn$ calcd.: C, 64.3; H, 3.90; N, 4.99%.)

The preparation of the solid triphenyltin(IV) oxinate was effected essentially as shown in ref. 2, with only little variation. One or two mmoles of both the solids (the organotin chloride and *S*-quinolinol) were mixed and dissolved in about 100–200 ml of 95% hot ethanol (warmed to about 50°C). The complex was then precipitated by addition of a small quantity of a solution of sodium acetate in aqueous ethanol followed by ammonia. Recrystallization from ethanol gave a yellow crystalline solid, m.p. 145–146.5°. (Found: C, 64.34; H, 4.21; N, 2.86. $C_{27}H_{21}NOSn$ calcd.: C, 65.5; H, 4.2; N, 2.83%.)

The analysis of these solids was carried out by the usual methods. The absence of chloride ion in both the solids was verified.

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The absorption data were measured on Beckman model D.U. spectrophotometer, using 1-cm cells. The solutions investigated were prepared by dissolving the solid oxinates in 95 % ethanol. The reference liquid was 95 % ethanol. The concentrations of the solutions were such as to give optical densities in the range 0.15–0.85.

RESULTS

The absorption spectra are reported in Fig. 1 as $\log \epsilon$ (*viz.* the logarithm of the molecular extinction coefficient) against the wavelength, λ , in $m\mu$. These $\log \epsilon$ data are average values calculated from optical density readings on a number of solutions taken from several stocks $3 \cdot 10^{-4}$ M. The latter were obtained by dissolving in 95 % ethanol the various solid samples prepared by us.

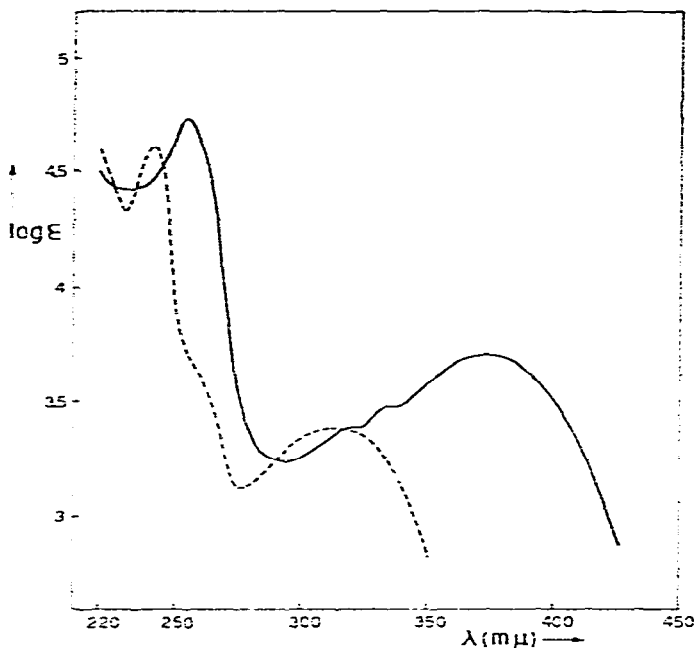


Fig. 1. Absorption spectra of $(C_6H_5)_2Sn-(oxinate)$ and $(C_6H_5)_2Sn-(oxinate)_2$ in 95 % ethanol. The logarithm of the molecular extinction coefficient, $\log \epsilon$, plotted against the wavelength, λ in $m\mu$. (---) = $(C_6H_5)_3Sn-(oxinate)$; (—) = $(C_6H_5)_2Sn-(oxinate)_2$.

The oxinates obey the Beer's law in all the range of wavelengths examined.

The molecular extinction coefficients of the organotin oxinates in 95 % ethanol at absorption maxima are reported in Table I, together with the data for 8-quinolinol and 8-quinolinium ion in the same solvent system as given by Ohnesorge and Rogers³.

DISCUSSION

The absorption spectrum of the diphenyltin(IV) dioxinate is very similar to those of many metal oxinates (see ref. 3 and Fig. 1 of this work). It corresponds to the spectrum of the 8-quinolinium cation (see Table I). In addition the molecular extinction coeffi-

cient at 375 $m\mu$ of the diphenyltin(IV) derivative is about twofold the value of ϵ -quinolinol in 95% ethanol at 313 $m\mu$ (see Table 1).

TABLE I
ABSORPTION DATA OF DIPHENYLTIN DIOXINATE, TRIPHENYLTIN OXINATE AND
 ϵ -QUINOLINOL* IN 95% ETHANOL SOLUTIONS

Compound	Solvent	Wavelengths of absorption maxima (λ , $m\mu$) and corresponding molecular extinction coefficients (ϵ)							
		λ	$\epsilon \cdot 10^{-3}$	λ	$\epsilon \cdot 10^{-3}$	λ	$\epsilon \cdot 10^{-3}$	λ	$\epsilon \cdot 10^{-3}$
$(C_6H_5)_2Sn$ -(oxinate) ₂ S-quinolinol	95% ethanol	255	53.4	320	2.43	334	2.99	375	5.09
	0.01 N HCl in 95% ethanol	254	68	310	1.8	321	1.6	365	2.2
$(C_6H_5)_3Sn$ -(oxinate) S-quinolinol	95% ethanol	242	40.3	313	2.42				
	95% ethanol	241	68	313	2.6				

* As given by Ohnesorge and Rogers³.

From these data it seems that $(C_6H_5)_2Sn$ -(oxinate)₂ is a chelate complex^{4,5} with the tin atom covalently bonded to the oxygen and nitrogen atoms of chelating ϵ -quinolinol⁶. In this complex the coordination number of the tin atom would be six, and the most probable stereochemical distribution is octahedral. Similar suggestions have been made for $(CH_3)_2SnCl_2$ complexes by Beattie and McQuillan⁷ who showed, by means of infrared spectra, that the compounds $(CH_3)_2SnCl_2-L$ ($L = 1,10$ -phenanthroline and 2,2'-bipyridyl) are chelated complexes and that the tin atom is six-coordinated. The same was found for the compounds CH_3SnCl_3-L ($L = 1,10$ -phenanthroline and 2,2'-bipyridyl)⁷.

The tendency of the tin atom in diorganotin compounds to become six-coordinated in chelate complexes is shown also by the existence of the chelate complex $(CH_3)_2SnL_2$ ($L =$ acetylacetonate)⁸ and also of compounds of the type R_2SnX_2-L ($R =$ methyl, ethyl, butyl, octyl, phenyl; $X =$ halide or thiocyanate; $L = 1,10$ -phenanthroline and 2,2'-bipyridyl)^{2,7,9} [assuming that they are all chelated; the $(CH_3)_2SnCl_2$ derivatives are known⁷ to be]. It can be concluded that the tin atom in the R_2Sn^{2+} cations and R_2SnCl_2 compounds usually exhibits a maximum coordination number of six in chelate complexes, in accordance with our findings on diphenyltin(IV) dioxinate.

The formation of organotin complexes with a coordination number lower than six, which is the predominant behaviour in certain solvent systems, obviously cannot be excluded; this is the case of the $(CH_3)_2Sn^{2+}$ complexes with 1,10-phenanthroline, acetylacetonate and picolinate ligands in aqueous solutions, which have the formula $(CH_3)_2SnL$, the central tin atom being four-coordinated⁸.

The absorption spectrum of the triphenyltin(IV) oxinate in 95% ethanol is quite different from that of diphenyltin(IV) dioxinate (see Fig. 1). It corresponds exactly to that of ϵ -quinolinol in the same solvent, both for the wavelengths and the molecular extinction coefficients of the absorption bands, and the similarity between the two spectra is maintained when HCl or NaOH is added to the ethanolic ϵ -quinolinol and triphenyltin(IV) oxinate. This suggests that the nitrogen atom of the ligand does not bond the tin atom of the organotin cation, and that the triphenyltin(IV) oxinate

is not a chelate complex. The tin atom is thus bound, more or less covalently, to the oxygen atom of the δ -quinolinol, presumably with a tetrahedral bond distribution.

It is interesting to consider why the tin atom in this compound is not five-coordinated, while it is known that the compounds R_3SnX usually form the five-coordinated complexes R_3SnX-L with monodentate ligands L ; this has been shown for the complex $(CH_3)_3SnCl$ -pyridine by X-ray diffraction studies which revealed that the complex is a trigonal bipyramid¹⁰. Similar structures can be advanced for other complexes of R_3SnX compounds with unidentate ligands¹¹. On the other hand, it is known that the compound $(CH_3)_3SnCl$ fails to form chelate complexes with 1,10-phenanthroline and 2,2'-bipyridyl⁷. The reluctance of the tin atom of R_3SnX compounds and R_3Sn^+ cations to give five-coordinated or six-coordinated compounds by chelation can perhaps be attributed to steric hindrance.

Finally we consider the possibility of analytical applications. Methods of spectrophotometric determinations of $(C_6H_5)_2Sn^{2+}$ by δ -quinolinol may be readily developed. The presence of $(C_6H_5)_3Sn^+$ does not reduce the accuracy, because its oxinate does not absorb appreciably at the longer wavelengths absorption maximum of the diphenyltin(IV) derivative (see Fig. 1). If other organotin cations, R_2Sn^{2+} , behave like $(C_6H_5)_2Sn^{2+}$ cations towards δ -quinolinol, then micromethods can probably be developed for their determination through their δ -quinolinol complexes.

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SUMMARY

The complexes formed between diphenyltin(IV) and triphenyltin(IV) cations and δ -quinolinol were prepared and studied spectrophotometrically in ethanol solution. It was shown that diphenyltin dioxinate is very probably a chelate complex, with a coordination number of six for the tin atom, and that triphenyltin oxinate probably is not a chelate complex, and has a coordination number of four for the tin atom.

Triphenyltin oxinate has been prepared in the solid state for the first time.

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