Organotin oxinates containing a penta-coordinated tin atom

Triphenyltin oxinate has been studied spectroscopically by Roncucci *et al.*[1]. They proposed that the compound is not a chelate complex and has a coordination number of four for the tin atom, although diphenyltin dioxinate is a chelate complex with a coordination number of six. These findings were derived from the similarity of the spectra of an aqueous alcohol solution of triphenyltin oxinate to that of 8-quinolinol and of diphenyltin oxinate to those of various metal oxinates.

This observation at first sight, however, is inconsistent with the fact that triphenyltin oxinate has yellow color as is described in their report, while 8-quinolinol in the pure state is a colorless, crystalline compound. During the study of organotin complexes[2-7] in our laboratory, some evidence for a chelate structure for triphenyltin oxinate has now been obtained.

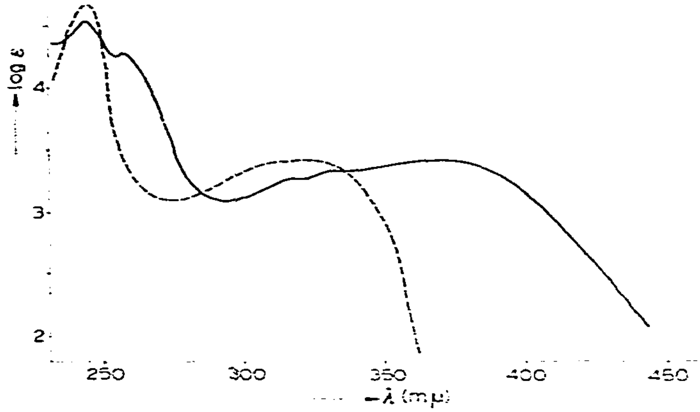
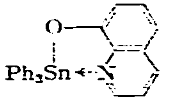
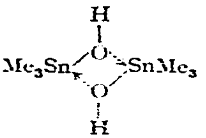


Fig. 1. Absorption spectra of 8-quinolinol and triphenyltin oxinate in cyclohexane. The logarithm of the molecular extinction coefficient, log ε, plotted against the wavelength, λ in mμ. --------, 8-quinolinol; — —, $(C_6H_5)_2Sn(ox)$.

A solution of triphenyltin oxinate in cyclohexane is yellow, and the electronic spectrum (Fig. 1) shows a ligand band at *ca.* 370 mμ with long tailing toward the visible region. This absorption band position corresponds exactly to those of various chelated metal oxinates at 370–430 mμ[8], rather than to that of 8-quinolinol at *ca.* 320 mμ in cyclohexane. A molecular weight determination of triphenyltin oxinate by cryoscopic method gave a value in cyclohexane and in benzene corresponding to a monomer, indicating that *inter*molecular coordination of the oxinate ligand did not occur. We, therefore, believe that the compound has the chelate structure (I) in cyclohexane and, probably, even in the solid state.



Triphenyltin oxinate (I)



Trimethyltin hydroxide (II)

The discrepancy between the observations of the Italian chemists[1] and ours might be caused by the hydrolysis of the compound on solution, in the aqueous ethanol medium which they used. An analogous case is seen in trimethyltin hydroxide in solution[9]. This compound (II) is dimeric in a rigorously anhydrous solvent, but suffers facile hydrolysis in a wet solvent.

Dialkyltin halide oxinates, $XR_2Sn(ox)$ ($X = Cl, NCS$), were prepared by the reaction of dialkyltin dihalide and 8-quinolinol in absolute alcohol or by the reaction of dialkyltin dihalide and dialkyltin dioxinate in absolute alcohol. For example: *dimethyltin chloride oxinate*, (m.p. 135–136.5°. Found: C, 40.41; H, 3.76; Cl, 10.56; N, 4.29; Sn, 35.95. $C_{11}H_{12}ClNOSn$ calcd.: C, 40.24; H, 3.68; Cl, 10.86; N, 4.24; Sn, 36.15 %.), *dimethyltin isothiocyanate oxinate*, (m.p. 123–124°. Found: C, 40.92; H, 3.45; N, 8.16. $C_{12}H_{12}N_2OSSn$ calcd.: C, 41.06; H, 3.45; N, 7.98 %.), or *di-n-propyltin isothiocyanate oxinate* (m.p. 144°. Found: C, 47.39; H, 4.78; N, 6.89; S, 7.63. $C_{16}H_{20}N_2OSSn$ calcd.: C, 47.21; H, 4.95; N, 6.88; S, 7.88 %.), are also yellow crystalline compounds, and may contain a penta-coordinated tin atom.

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

MASANORI WADA
KATSUHIKO KAWAKAMI
ROKURO OKAWARA

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The effect of dipolar aprotic solvents on quadrupole splitting of Mössbauer spectral lines of dibutyltin dichloride

In recent years there has been an increasing interest in the effect of solvents on organic reactions. One of the most active areas in this field is the use of dipolar aprotic solvents that strongly solvate cations but poorly (predominantly electrostatically) solvate anions.

Electron-donating aprotic solvents such as dimethylformamide (DMFA), dimethyl sulfoxide (DMSO) and hexamethyltriamidophosphate (HMTAP) do not form hydrogen bonds with anions but interact rather strongly with electron-deficient cations. This results in the poorly solvated anions having very high reactivity in nucleophilic reactions (type S_N2). Reviews dealing with the outstanding role which solvating aprotic solvents play in a great many organic reactions have been published recently[1–3]. Ethers such as tetrahydrofuran (THF) and dimethoxyethane (DME) can be regarded as solvents of this type[3,4]. The solvation effect of THF and DME in metal-organic reactions is rather marked and commensurable with those of DMFA, DMSO, etc.

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