

Molecular Adducts of Triphenyltin(ethylxanthate)

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A few 1:1 molecular adducts of $\text{Ph}_3\text{SnSC}(\text{S})\text{OC}_2\text{H}_5$ with some aromatic amine N-oxides have been prepared and characterised.

A few organometal xanthates have been reported¹⁻³, but their acceptor properties have not been investigated. The present note deals with the synthesis of hitherto unknown adducts of the formula $\text{Ph}_3\text{SnSC}(\text{S})\text{OC}_2\text{H}_5\cdot\text{L}$ (where L = PyO, 3-picO, 4-picO, QuO, BiPyO₂).

Triphenyltin(ethyl xanthate) was prepared by metathetical reaction between triphenyltin chloride⁴ and potassium ethyl xanthate⁵ in 1:1 molar ratio. The adducts were prepared as follows:

To a stirred solution of triphenyltin(ethyl xanthate) (2.35 g, 5 mmol) in anhydrous dichloromethane (30 ml) was added a solution of aromatic amine N-oxide (10 mmol) in the same solvent (20 ml) and refluxed for 5 hr. Excess solvent was distilled off and the residual solution kept overnight in a deep freeze to yield a crystalline solid, which recrystallised from dichloromethane-pet ether (1:2).

The complexes are white crystalline sharp melting solids, stable in dry inert atmosphere at room temperature. They are soluble in common organic solvents. Molecular weight determination in benzene (Table 1) and conductivity measurements in nitrobenzene (2.41-3.01 mho $\text{cm}^2\text{mol}^{-1}$) indicate the adducts to be monomeric and nonelectrolytes.

The IR spectrum of the triphenyltin (ethyl xanthate) exhibits peaks in the region 1260-1210 and 1150 cm^{-1} due to $\nu(\text{C}-\text{O}-\text{C})$, indicating that one C—O bond is stronger than the other suggesting the bidentate character of the xanthate group^{2,6-7}. Similarly the presence of a single band in the region 1100-1000 cm^{-1} due to $\nu(\text{C}-\text{S})$ also indicates its bidentate character⁸. A few absorptions of weak to medium intensity observed at 400 ± 5 , 380 ± 5 and 265 ± 5 cm^{-1} are assigned to $\nu(\text{Sn}-\text{O})$, $\nu(\text{Sn}-\text{S})$ and $\nu(\text{Sn}-\text{Ph})$ modes⁹ respectively. The IR spectra of aromatic N-oxides display a band of strong intensity in the region 1265-1210 cm^{-1} due to $\nu(\text{N}-\text{O})$. This band undergoes

Table 1 – Analytical Data of
 $\text{Ph}_3\text{SnSC}(\text{S})\text{OC}_2\text{H}_5\cdot\text{L}$ Complexes

L	m.p. (°C)	Yield (%)	Found(%) (Calc.)				Mol wt. found Calc.
			Sn	C	H	N	
3-PicO	160	70	20.2 (20.5)	56.0 (55.9)	4.4 (4.6)	2.3 (2.4)	540 (580)
4-picO	150	78	20.3 (20.5)	55.6 (55.9)	4.8 (4.6)	2.3 (2.4)	540 (580)
PyO	135	82	21.1 (20.9)	55.2 (55.1)	4.3 (4.4)	2.4 (2.5)	520 (566)
QuO	175	67	19.2 (19.3)	58.4 (58.5)	4.2 (4.3)	2.3 (2.3)	580 (616)
BipyO ₂	145	74	17.9 (18.0)	56.3 (56.5)	4.2 (4.2)	4.3 (4.2)	627 (659)

considerable negative shift ($-\Delta\nu = 25-55$ cm^{-1}) on complexation indicating coordination from the oxygen atom of the base to the tin atom¹⁰.

PMR spectrum of one of the compounds $\text{Ph}_3\text{SnSC}(\text{S})\text{OC}_2\text{H}_5\cdot\text{ONC}_5\text{H}_4\text{CH}_3 - 3$ was recorded in CDCl_3 at 30°C. The compound exhibits a multiplet (19H) in the region $\delta 8.10-7.20$, due to aromatic protons. CH_2 and CH_3 protons of the ethyl xanthate moiety appear as a quartet at 4.5 (2H) and a triplet at 1.42 (3H). The singlet due to CH_3 group of the coordinated 3-picoline N-oxide is centered at $\delta 2.20$. The spectrum and its integration are consistent with the proposed (1:1) stoichiometry of the adduct. An octahedral geometry around hexa-coordinated tin atom is tentatively proposed.

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