

Synthesis and structural characterization of 2-(arylozo)pyridine triphenyltin(IV) perchlorate

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A few complexes of the composition $[\text{Sn}(\text{C}_6\text{H}_5)_3(\text{L})]\text{ClO}_4$ have been synthesized and characterized on the basis of IR, ^{119}Sn Mössbauer and NMR studies. The spectroscopic data suggest that the complexes exist in meridional-trigonal bipyramidal (mer-SnPh₃NN) geometry.

Recently, we have reported a series of organotin(IV) perchlorate complexes of the types - (I): $[\text{Sn}(\text{R}_3)(\text{L}_2)]\text{ClO}_4$ (ref. 1) (where R = ⁿBu or Ph; L = pyridine, γ -picoline, 2,2'-bipyridine and 1,10-phenanthroline), (II): $[\text{Sn}(\text{R}_2)(\text{L}_n)](\text{ClO}_4)_2$ (ref. 2) (where R = Me or Ph; L = pyridine, quinoline, 2,2'-bipyridine and 1,10-phenanthroline) and (III): $[\text{Sn}(\text{R}_2)(\text{L}_2)](\text{ClO}_4)_2$ (ref. 3) (where R = Me; L = substituted 2-(arylozo) pyridine. These complexes possess interesting structural motifs viz., trans-trigonal bipyramidal geometry in (I) while distorted trans-R₂Sn octahedral in (II) and (III). As a part of our ongoing structural studies on organotin(IV) perchlorate complexes¹⁻³, we now report meridional-trigonal bipyramidal arrangement around tin in $[\text{Sn}(\text{C}_6\text{H}_5)_3(\text{L})]\text{ClO}_4$ from their IR and Mössbauer data in solid state.

Experimental

A freshly prepared Ph₃SnClO₄ was used throughout the investigation¹. The ligands viz., 2-(arylozo) - (L¹), 2-(*m*-tolylazo) - (L²), 2-(*p*-tolylazo) - (L³), 2-(*p*-chlorophenylazo) - (L⁴) pyridine were prepared by the method reported earlier³⁻⁵ while 2-[*p*-(dimethylamino)phenylazo] pyridine (L⁵) was an Aldrich reagent. Precautions were taken to exclude moisture. Care in handling the perchlorate complexes have been exercised. The m.p.s. were not determined owing to unknown nature of the perchlorates.

The IR, NMR and ^{119}Sn Mössbauer spectral measurements were carried out as previously described¹⁻⁵.

Synthesis of $[\text{Sn}(\text{C}_6\text{H}_5)_3(\text{L}^4)]\text{ClO}_4$ [4]

A solution of L⁴ (0.50 g, 2.29 mmol) in ethanol (20 ml) was added dropwise with constant stirring to a freshly prepared solution of Ph₃SnClO₄ (1.03 g, 2.29 mmol) in benzene-ethanol mixture (20 + 25 ml) and the resulting solution refluxed for 6h. The excess solvent was slowly distilled off and the resulting product obtained as a resinous mass which was washed thoroughly with pet. ether. Then, the resinous material in 20 ml of pet. ether was cooled in an ice-bath and subsequent scratching yielded the desired product, filtered, washed with pet. ether and dried *in vacuo*; yield 80 %. [Found : C, 52.26; H, 3.50; N, 6.30; Sn, 17.70. Req'd. for C₂₉H₂₃N₃O₄Cl₂Sn : C, 52.19; H, 3.45; N, 6.30; Sn, 17.80 %; Λ_M (CH₃CN) : 140 ohm⁻¹ cm²mol⁻¹].

The other derivatives were prepared similarly using the appropriate ligand.

$[\text{Sn}(\text{C}_6\text{H}_5)_3(\text{L}^1)]\text{ClO}_4$ [1]; yield, 72 %. [Found : C, 55.00; H, 3.80; N, 6.70; Sn, 18.70. Req'd. for C₂₉H₂₄N₃O₄ClSn : C, 55.04; H, 3.79; N, 6.64; Sn, 18.77 %; Λ_M (CH₃CN) : 130 ohm⁻¹ cm²mol⁻¹].

$[\text{Sn}(\text{C}_6\text{H}_5)_3(\text{L}^2)]\text{ClO}_4$ [2]; yield 78%. [Found : C, 55.80; H, 4.00; N, 6.50; Sn, 18.20. Req'd. for C₃₀H₂₆N₃O₄ClSn : C, 55.71; H, 4.02; N, 6.49; Sn, 18.37 %; Λ_M (CH₃CN) : 145 ohm⁻¹ cm²mol⁻¹].

$[\text{Sn}(\text{C}_6\text{H}_5)_3(\text{L}^3)]\text{ClO}_4$ [3]; yield 75%. [Found : C, 55.60; H, 4.10; N, 6.52; Sn, 18.10. Req'd. for C₃₀H₂₆N₃O₄ClSn : C, 55.71; H, 4.02; N, 6.49; Sn, 18.37 %; Λ_M (CH₃CN) : 144 ohm⁻¹ cm²mol⁻¹].

$[\text{Sn}(\text{C}_6\text{H}_5)_3(\text{L}^5)]\text{ClO}_4$ [5]; yield 70%. [Found : C, 55.10; H, 4.30; N, 8.30; Sn, 17.60. Req'd. for C₃₁H₂₉N₄O₄ClSn : C, 55.09; H, 4.29; N, 8.29; Sn, 17.58 %; Λ_M (CH₃CN) : 121 ohm⁻¹ cm²mol⁻¹].

Results and discussion

The reagent Ph₃SnClO₄ reacts smoothly with 2-(arylozo)pyridine in boiling benzene-ethanol mixture in the ratio 1:1 to yield cationic complexes of the type $[\text{Sn}(\text{C}_6\text{H}_5)_3(\text{L})]^+$ which have been isolated as perchlorate salts from the reaction mixture in high yields. The complexes are brown to orange, stable and nonexplosive atleast at ordinary temperature. The molar conductance data in acetonitrile lies between 121-145 ohm⁻¹ cm²mol⁻¹, suggesting a 1:1 type of electrolytic nature of the complexes in accordance with our earlier observation¹.

Table 1— ^{119}Sn Mössbauer data (mm s^{-1})^a of the complexes

Complex	I.S.	Q.S.	$\Gamma \pm$
[1]	1.31	3.38	0.90
[2]	1.32	3.38	0.88
[4]	1.30	3.36	0.87

^aIsomer shift with respect to R.T. Ca $^{119}\text{SnO}_3$, and nuclear quadrupole splitting, both at liquid nitrogen temperature.

The 2-(arylozo) pyridine ligands exist as stable *trans*- isomeric forms and possess azo- and pyridine nitrogen atoms, both able to coordinate to tin³⁻⁵. In view of these informations, the mode of coordination of the complexes is sought from their diagnostically important IR, ^1H NMR and ^{119}Sn Mössbauer spectra. Several features of the infrared spectrum of $[\text{Sn}(\text{C}_6\text{H}_5)_3(\text{L})]\text{ClO}_4$ are noteworthy. The coordination through pyridine and azo- nitrogen atom would be expected to lead to a shift of $\nu(\text{C}=\text{N})$ and $\nu(\text{N}=\text{N})$ bands. In the spectra of complexes, the band due to $\nu(\text{C}=\text{N})$ at $\sim 1580\text{ cm}^{-1}$ (ligand) is shifted to $\sim 1590\text{ cm}^{-1}$, indicating coordination by pyridine nitrogen atom³⁻⁵. The shift of ligand $\nu(\text{N}=\text{N})$ band (1420 cm^{-1}) to lower wavenumber in the complexes at $\sim 1385\text{ cm}^{-1}$, confirms the participation of one of the azo-nitrogens in the coordination. Thus, the ligand behaves in a bidentate manner^{3,4}. The complexes also exhibit broad structureless band centered at 1110 cm^{-1} due to $\nu(\text{ClO}_4)_{\text{as}}$, which suggests the lack of significant perchlorate coordination¹⁻³. In the low frequency infrared region, the appearance of the medium intensity bands at 270 and 240 cm^{-1} in the complexes is assigned to the $\nu_{\text{as}}\text{ Sn-C(Ph)}$ and $\nu_{\text{s}}\text{ Sn-C(Ph)}$, respectively^{1,6,7}. Thus the above discussion suggests that the bidentate ligand coordinate to the organotin counterpart while perchlorate ion resides outside the coordination sphere.

The ^1H NMR spectra of the complexes in $\text{DMSO}-d_6$ supported the proposed stoichiometry of the complexes. The ligand H-6 proton (proton adjacent to pyridine nitrogen atom) were sensitive to coordination and shifted downfield by 0.1 ppm in comparison with those in the free ligand. Such substantially smaller shift could be attributed to weak Sn-N interaction in solution. Further evidence in support of the structure is obtained from the ^{119}Sn Mössbauer spectra in the solid state (Table 1). The Mössbauer data of the complexes lie inside the range delimited for five coordinate triorganotin complexes⁸. The observed quadrupole splitting (Q.S.) values are close to *trans*- and meridional- R_3SnX_2 geometry. At this stage, it must be borne in mind that the neutral $\text{Ph}_3\text{SnCl.L}$ [$\text{L} = 2\text{-(arylozo)pyridine}$] complexes have recently

been assigned to *trans*- trigonal bipyramidal geometry in the solid state and in solution⁵ where the Q.S. values were 2.83 mm s^{-1} . A similar conclusion has been made on the organotin(IV) perchlorate complexes of the type (I) (ref. 1). Thus the Q.S. values (3.38 mm s^{-1}) for the complexes of the present study are obviously quite different, indicating a gross change from the structure of its triphenyltin perchlorate analogue (I) which could be due to steric demands of 2-(arylozo)pyridine ligand to adopt a meridional- geometry rather than the *trans*- structure. Although the observed values are slightly lower than that for the regular meridional-geometry, it may be ascribed due to considerable distortion of the SnPh_3 framework. However, such geometry has also been proposed for triorganotin complexes of N,O donor azo-ligands^{9,10} where the Q.S. values were $\sim 3.0\text{ mm s}^{-1}$.

In general, all the complexes exhibit similar Q.S. values, corroborating that the complexes are isostructural. The observed isomer shifts (I.S.) are 1.30 mm s^{-1} and are typical of quadrivalent tin in organometallic compounds¹¹. The full width of half maximum ($\Gamma \pm$) of these resonance absorptions are approximately 0.90 mm s^{-1} , which further suggests the presence of a single tin atom in the structure.

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