

Triorganotin(IV) Halide Complexes of Tetrakis(nitroindazolyl)borates

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Cationic trialkyl tin complexes of the type R_3SnL , where R = methyl, phenyl and butyl; and L = potassium tetrakis (5-nitroindazolyl) borate and potassium tetrakis (6-nitroindazolyl) borate (counter anion ligands) have been prepared. The complexes have been found to have a 1:1 (metal to ligand) ratio. Their molar conductivity values indicate their non-ionic character. An octahedral geometry has been proposed for all the complexes in which six-coordinated tin is bonded to three alkyl groups and three indazolyl groups.

The chemistry of organoborates has developed due to the pioneering work of Trofimenko¹⁻³, who prepared a series of poly (pyrazolyl) borates. In our laboratory, synthesis of analogous series of compounds, poly (1-indazolyl) borate^{4,5} and poly (5- and 6-nitroindazolyl) borate^{7,8}, has been achieved and their complexes with transition metal ions have been studied. However, such work does not seem to have been done on triorganotin (IV) halides. The study of organotin (IV) complexes has become a subject of current research interest because of their biocidal activity^{9,10}. We report here the preparation and characterisation of triorganotin (IV) halide complexes of tetrakis (nitroindazolyl) borates.

Trimethyltin chloride, triphenyltin chloride (Fluka), tributyltin chloride (E. Merck), 5-nitroindazole and 6-nitroindazole (Koch-Light) and potassium borohyd-

ride (BDH) were used as received. The IR spectra in KBr and far IR spectra in nujol were recorded on a Perkin-Elmer 621 spectrophotometer. C, H and N were microanalysed and chlorine was estimated gravimetrically. Conductivity measurements were made on a Systronics conductivity bridge type 302.

Preparation of the complexes

Potassium tetrakis (5-nitroindazolyl) borate and potassium tetrakis (6-nitroindazolyl) borate were prepared by known methods^{7,8}. Owing to the non-availability of the solid tetrakis ligands, the complexes were synthesized by using the ligand suspensions in DMF.

Complexation was carried out by pouring an ice-cold suspension of the ligand (1 g, 0.00143 mol) in 20 ml of DMF into ice-cold triphenyltin chloride (0.466 g, 0.00143 mol), tributyltin chloride (0.551 g, 0.00143 mol) or trimethyltin chloride (0.2853 g, 0.00143 mol) taken in 20 ml of ethanol. The contents were stirred for about six hours at 0°C. The solid complexes which separated out after a week were filtered, washed with alcohol and dried *in vacuo*.

The composition of the complexes was established on the basis of elemental analyses. All the complexes were found to have 1:1 (M:L) ratio. Their melting points and analytical data are given in the Table 1. A very low molar conductance value of $10^{-3} M$ solution in methanol (0.0029-0.0075 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$) suggests non-ionic nature of these compounds.

The mode of the bonding was studied on the basis of the changes in the IR spectra on complex formation. The IR spectral bands observed in high frequency region are due to the heterocyclic and the aromatic

Table 1—Characterisation Data of Trialkyl Tin (IV) Halide Complexes

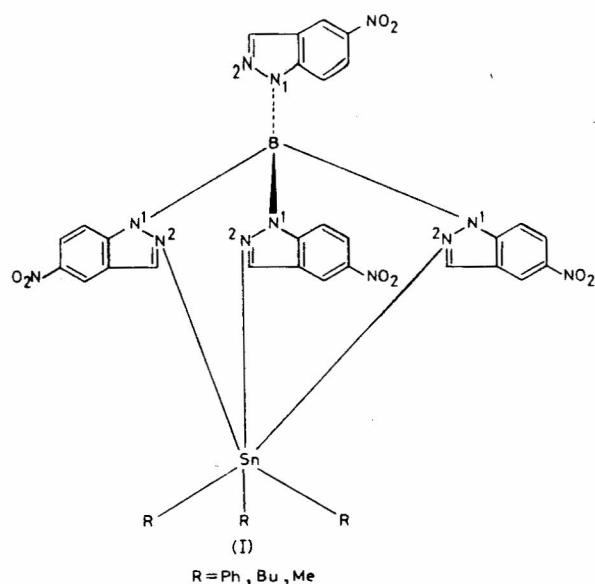
Complexes	m.p. (°C)	Colour	Yield (%)	Found (Calc), %			
				C	H	N	Sn
$\text{Ph}_3\text{SnB}(5\text{-nitro In})_4$	70	Yellow	43	55.04 (54.76)	3.52 (3.07)	15.89 (16.66)	11.60 (11.70)
$\text{Bu}_3\text{SnB}(5\text{-nitro In})_4$	95	Brown	55	51.07 (50.60)	5.00 (5.06)	18.02 (17.72)	12.42 (12.44)
$\text{Me}_3\text{SnB}(5\text{-nitro In})_4$	111	Light brown	48	45.06 (45.25)	3.54 (3.04)	20.23 (20.47)	14.22 (14.35)
$\text{Ph}_3\text{SnB}(6\text{-nitro In})_4$	64	Brown	50	57.45 (57.67)	3.04 (3.11)	16.60 (16.72)	11.54 (11.68)
$\text{Bu}_3\text{SnB}(6\text{-nitro In})_4$	80	Dark brown	60	53.95 (52.85)	3.16 (3.09)	17.04 (17.11)	12.47 (12.59)
$\text{Me}_3\text{SnB}(6\text{-nitro In})_4$	109	Brown	40	46.85 (46.02)	3.16 (3.21)	20.40 (20.32)	14.32 (14.41)

parts of the ligand. A slight shift is observed for some of the bonds after coordination which offers some evidence for the assignment of the probable coordination sites. A weak band at 1390 cm^{-1} in potassium (5-nitroindazolyl) borate and at 1380 cm^{-1} in potassium (6-nitroindazolyl) borate has been assigned to $\nu\text{B}-\text{N}$; it undergoes very little change on complex formation. Similarly, νNO_2 frequency, observed as a strong band at 1500 cm^{-1} in potassium (5-nitroindazolyl) borate and at 1520 cm^{-1} in potassium (6-nitroindazolyl) borate, also remains almost unaltered after coordination with the tin moiety. These results indicate that neither the nitro group nor the nitrogens bonded to boron (N-1) are involved in coordination with the tin atom.

A negative shift of about $15\text{-}35\text{ cm}^{-1}$ in $\nu\text{C}=\text{N}$ frequency^{12,13} in the case of potassium (5-nitroindazolyl) borate has been observed suggesting that only tertiary nitrogens (N-2) of the tetrakis (nitroindazolyl) borate are involved in coordination.

The IR spectra of $\text{Ph}_3\text{SnB}(\text{5-nitro In})_4$ and $\text{Ph}_3\text{SnB}(\text{6-nitro In})_4$ in the low frequency region show bands at 275 and 235 cm^{-1} which have been assigned to the $\nu\text{Sn}-\text{Ph}$ and $\nu\text{Sn}-\text{Ph}$ frequencies of the triorganotin moiety. It has been found that the positions of these $\text{Ph}-\text{Sn}$ bands remain unaltered when Sn atom undergoes a change in its coordination number as reported in the case of $\text{Ph}_3\text{SnCl}^{14}$. A medium intensity band observed in the region $470\text{-}380\text{ cm}^{-1}$ in the spectra of the complexes is presumably due to $\text{Sn}-\text{N}$ stretching frequency¹¹.

It is clear that only 1:1 complexes of R_3SnCl with the K^+ salts of both the anionic ligands are formed by the substitution of K^+ by the cation R_3Sn^+ . The ligands have four tertiary nitrogen atoms (N-2) in the nitroindazole moiety attached to boron, but all of them may not be coordinated to the metal in view of the tetrahedral disposition of the four nitroindazolyl groups containing these nitrogen atoms around the boron atom. It is most likely that the Sn atom is coordinated to only three of these nitrogens, and the Sn atom achieves hexa-coordination assuming an octahedral geometry (Structure I).



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