Abstract
SYNTHESSES AND PHYSICO-CHEMICAL STUDIES ON ORGANOTIN DERIVATIVES OF POLYORGANYL BORATES

ABSTRACT

The pioneering work of Trofimenko on the ligands of pyrazole, imidazole and benzimidazole have generated considerable interest in the last few decades. Work on the synthesis of some boron nitrogen ligands and their transition metal complexes has been reported from our laboratory. Of particular interest to the present study is hydrotris (pyrazolyl) borate \([\text{HB(pz)}_3]^-\) as it forces higher than normal coordination and may be used to prepare sandwich like compounds. It is a uninegative, tridentate, anionic ligand, constrained to occupy three adjacent positions of an octahedral coordination sphere. This ligand has been used extensively to provide a number of notable complexes of the transition metals.

Two types of complexes i.e. five-coordinated \(\text{R}_3\text{SnL} \quad (\text{R} = \text{C}_4\text{H}_9\) and \(\text{C}_6\text{H}_5\) and \(\text{L} = \{\text{HB(pz)}_3\}^-\) and six-coordinated \(\text{R}_2'\text{SnL}_2 \quad (\text{R}' = \text{CH}_3, \text{C}_4\text{H}_9\) and \(\text{L} = \{\text{HB(pz)}_3\}^-\) have been prepared from the appropriate organotin/chlorides and \(\text{K}[\text{HB(pz)}_3]\) in dichloro methane. These complexes were characterized by melting points, elemental analyses, infra red and proton NMR spectroscopy and conductance measurements.

The compositions of the synthesized complexes have been ascertained by elemental analyses. However, the IR spectra show an insignificant shifting in B-N, frequencies suggesting a coordination through the pyridyl nitrogen. The tentative assignment
of Sn-N stretching vibration in the region 350-450 cm\(^{-1}\) has also been made. The proton NMR spectra of the complexes shows equivalent atmosphere of all protons, of the pyrozole rings, even though one of the pyrazole ring is uncoordinated and suggests a rapid exchange between coordinated and uncoordinated rings.

In continuation of our work in the area of boron-nitrogen chemistry, the effect of the presence of methyl groups on pyrazole on the physico-chemical properties of organotin complexes was found interesting. The electron releasing nature of methyl groups should enhance the nucleophilicity of the ligand, making it a strong coordinating agent and providing new synthetic approaches for preparing such compounds. With this view, a series of organotin(IV) complexes with bi- and tridentate ligands containing methyl substituents on 3rd and 5th carbon of the pyrazolyl borate have been synthesized in dichloromethane. The compounds exhibited surprisingly high stability towards air and moisture. The IR spectra of the complexes show the geometry of the parent ligand is retained in the most of the cases. However, slight distortion is observed in organotin moiety with a bent C-Sn-C structure. The proton NMR spectra indicate Sn-R coupling effect on proton signals of organic group attached to the tin atom. The slight downfield shift in 3,5-dimethyl pyrazole ring suggest pyrazole-tin coordination.

The first isolation of spiroborate complexes was performed by Boeseken and co-workers, by synthesizing potassium bis catechol spiroborate from the reaction of catechol with potassium borate in water. We have studied same spiroborate with diphenols in non-aqueous media which has been obtained in good quantity.
The ligand has been found to be uninegative and bidentate. The formation of ligand is confirmed on the basis of elemental analyses data. Anionic ligand of this type is notable for its stability and ability to form complexes with organotins. A new series of 1:2 and 1:1 complexes of spiroborate with $R_3SnCl$ and $R'2SnCl_2$ have been prepared. The complexes $R_2SnL$ are pentacoordinated whereas $R_2SnL_2$ are hexa coordinated. The compounds are solid monomers. The high melting points show high thermal stabilities of complexes. The IR spectral studies suggest a square planar BO$_4$ moiety. The variation in the $\nu$(C-O) and $\nu$(B-O) indicate the coordination of ligand to the metal through oxygen. The presence of $\nu$(Sn-O) at 680 ± 10 cm$^{-1}$ confirms that the organotin-ligand linkage is covalent. The $^1$H NMR spectra show a significant downfield shift of the ring proton signals which suggests its coordination with electrophilic centre. Two sets of the ring proton signals appear due to slight hydrolysis of the complexes by the presence of water in NMR solvent. The ring proton signals were affected by addition of D$_2$O.

In order to assess hydrolic stability of Sn-O bond in the chelated spiroborate complexes and bond between Sn-S in presence of boron, a series of boron sulphur ligands were synthesized by the substitution of two and three hydrogen atoms of potassium boro hydride and by thiophenol corresponding to the formation of dihydrobis and hydrotris (thioly1) borate anions. The completion of the reaction was ascertained by the evolution of the corresponding amount of hydrogen gas. It has been found that the percentage yield was also affected by the solvent used in the