

Synthesis, Spectroscopic Characterization and Biological Studies of Organotin (IV) and Tin (II) Complexes of Some Schiff Base Ligands

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Abstract

The electronegativity of tin changes with its oxidation number, the lower oxidation state being connected with a more electropositive character. It may be concluded that tin (IV) compounds are more ionic than the corresponding tin (II) derivatives or from another point of view more electrophilic and thus, more tightly coordinated by the surrounding nucleophilic ligands.

The major difference between the structure of tin (II) and tin (IV) compounds (which may be ionic or covalent) can be seen in the coordination sphere of the tin atom. Tin (II) compounds are mostly bent, pyramidal or otherwise distorted, tin (IV) compounds adopt regular geometries as tetrahedral, bipyramidal or octahedral depending on the coordination number.

Tin is placed in the 4th group of the periodic table and belongs to the p block elements, preceded by indium and followed by antimony. The ground state electronic configuration of tin is $[\text{Kr}]^{36} 4d^{10} 5s^2 p^2$ and it has oxidation states +2 and +4. Zuckerman et al.^{70,71} have described the preparation and properties of tin (II) heterocycles in which the tin atom is in a five or seven membered ring. These compounds are crystalline solids of high thermal stability and are insoluble in most of the common organic solvents. Significantly, however, the heterocycles are slightly soluble in donor solvents such as

pyridine, which suggest that the molecules have an empty acceptor p-orbital on the tin atom as would be expected. The materials are monomeric in pyridine solution, but it is suggested that they may be polymeric in the solid state because of intermolecular tin oxygen bridging. The tin(II) heterocycles of many dihydric phenols have been obtained e.g. the biphenylenedioxytin(II) and o-phenylenedioxytin(II).

The Schiff base complexes of tin(II) moieties have also been investigated by Varshney et al.⁷²⁻⁷⁴ The interest in these complexes may also be ascribed to their novel structural features, which are possibly caused by the multidenticity of the Schiff base ligands. The tin(II) chelates with Schiff bases have been studied extensively on the basis of spectroscopic studies.

During the past few years, molecular complexes formed by the Lewis acid-base interaction of organotin moieties with primarily nitrogen and to a lesser extent phosphorous, oxygen and sulphur donor mono or polydentate ligands^{75,76} have been studied quite extensively. The complexes of the type $[\text{R}_n\text{SnX}_n\text{L}_2]$ (where n=2) generally show hexa-coordination with more or less distorted

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octahedral geometry around the tin atom depending on the nature of R,X and L with the possibility of *cis* and *trans*-isomerism.

Addition complexes of tin(IV) chloride with mono-functional bidentate Schiff bases of sulphadiazole

Reactions of stannic chloride with Schiff bases have been carried out in 1:2 molar ratio in ethanol medium as:



Where N NH represent the donor system of the Schiff bases. On stirring for about five hours, the resulting complexes were obtained as coloured solids mostly soluble in DMF, DMSO and CH₃OH. They were purified by repeated

washing with cyclohexane and their purity was further checked by TLC on silica gel-G with dry DMF as the solvent. The low molar conductance value of the complexes in DMF are in the range of 5-15 cm² mol⁻¹ indicating their non- electrolytic nature. All these complexes of tin(IV) are monomeric as evidenced by their molecular weight determination by the Rast camphor method.

IR Spectra

The ligands exhibit a broad and strong band in the region 3400-3150 cm⁻¹ due to νNH. In the spectra of the complexes, the band due to νNH vibration remains approximately in the same position, which clearly indicates the non- involvement of νNH in complexation. A strong band in the region 1600-1625 cm⁻¹ assignable to νC=N⁷⁹ is observed in all the ligands. A slight shift of this band towards the higher frequency region in the case of tin(IV) derivatives may be due to an increase in the bond order of the azomethine group.

Further, new strong bands in all the tin(IV) derivatives, appearing in the region 415-400 cm⁻¹ are due to the Sn N and Sn respectively⁸⁰.

¹H NMR Spectra

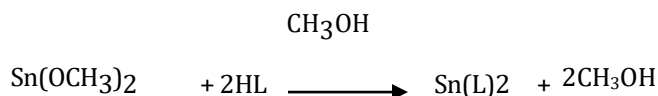
The ¹H NMR spectra of ligands show NH proton signals at ~10.09 ppm. The signal due to the NH proton remains unchanged in the compounds showing its non-involvement in coordination. A signal at 8.10 ppm is observed the, complexes due to the azomethine proton, which moves downfield in comparison to its original position in the free ligand, thereby indicating the coordination of the azomethine nitrogen to the tin atom. An appreciable change is also observed in the position of the aromatic phenyl protons appearing as a complex, multiple at 6.407.80 ppm.

¹⁹Sn NMR Spectra

The compounds SnCl₄(C₁₃H₁₄N₄O₂S₂)₂, SnCl₄(C₁₃H₁₄N₄O₃S)₂ give a signal at -292, -300 ppm. respectively in ¹¹⁹Sn NMR, indicative of six- coordination to the central tin atom and in agreement with previously reported values^{81,82}

Tin (II) complexes of Schiff bases of sulphadiazole

Tin (II) methoxide reacts with Schiff bases in equimolar ratio as shown below.



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Where HL represents the Schiff bases shown in Fig. On magnetically stirring for about 5 h the resulting complex are obtained as coloured solids. The molar conductance of a 10^{-3} M solution of the compounds in DMF ranges from 8-12 mol⁻¹ showing their non-electrolytic nature. The molecular weight determined by Rast camphor method reveals monomeric nature of the complexes.

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