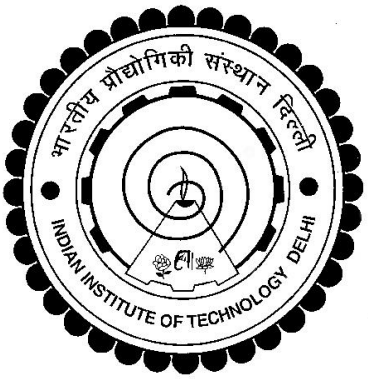
# SYNTHESIS AND CHARACTERIZATION OF DIORGANOTIN(IV) COORDINATION POLYMERS DERIVED FROM SILAALKYLPHOSPHONATE AND SULFONATE BASED LIGANDS

**NISHA SINGLA**




**DEPARTMENT OF CHEMISTRY**

**INDIAN INSTITUTE OF TECHNOLOGY DELHI**

**SEPTEMBER 2016**

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by

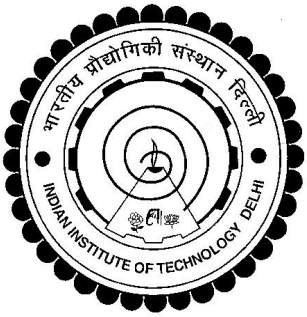
**NISHA SINGLA**

**Department of Chemistry**

**Submitted**

**In fulfillment of the requirements of the degree of Doctor of Philosophy**

**to the**




**INDIAN INSTITUTE OF TECHNOLOGY DELHI**

**SEPTEMBER 2016**

*Dedicated to My Family*

## CERTIFICATE

This is to certify that the thesis entitled "***Synthesis and characterization of diorganotin(IV) coordination polymers derived from silaalkylphosphonate and sulfonate based ligands***" being submitted by **Ms. Nisha Singla** to the Department of Chemistry, Indian Institute of Technology, Delhi, for the award of the degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her.

Nisha Singla has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma.

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NISHA SINGLA

## CONTENTS

# ABSTRACT

The work embodied in the thesis relates to the synthesis and structural studies of diorganotin(IV) based coordination assemblies derived from silaalkylphosphonic acids, $Me_3SiCH_2P(O)(OH)_2$, $R^1R^2_2Si(CH_2)_3P(O)(OH)_2$ ($R^1$, $R^2$ = Et; $R^1$ = Ph, $R^2$ = Me) and $Me_3SiC(CH_3)_2P(O)(OH)_2$. The choice of these ligands is driven by a desire to improve the solubility of the resulting coordination frameworks and take advantage of this property to transform the as-synthesized compounds into nano/colloidal domains using solution based approach. The thesis has been divided into five chapters.

Several diorganotin complexes of composition, $R_2Sn\{OP(O)(OH)(CH_2)_xSiR^1R^2_2\}(OSO_2Me)$ (**4-12**) have been synthesized by following the synthetic protocol reported earlier from our group. The X-ray crystallographic studies of a few such compounds reveal the formation of one-dimensional/layered/lamellar structural motifs, depending upon the nature of organic substituents on tin and phosphonate groups. The results are included in chapter III.

The incorporation of the silaalkylphosphonate groups in diorganotin(IV) phosphonates, $R_2Sn(O_3PCH_2SiMe_3)$ [R = Et (**13**), *n*-Bu (**14**)], $R_2Sn\{O_3P(CH_2)_3SiR^1R^2_2\}$ [$R^1$, $R^2$ = Et (**15**, **16**); $R^1$ = Ph, $R^2$ = Me (**17**, **18**)] and $Sn\{O_3P(CH_2)_xSiR^1R^2_2\}_2$ [x = 1, $R^1$, $R^2$ = Me (**19)**; x = 3; $R^1$, $R^2$ = Et (**20**), $R^1$ = Ph, $R^2$ = Me (**21)**] imparts ready solubility in common organic solvents including hydrocarbons and ethers. This property has been utilized to transform the as-synthesized compounds into nano/colloidal domains *via* ultrasonication of their solutions in ethanol-chloroform mixture. Depending upon the nature of the alkyl substituents on tin and phosphonate ligands, rod, disc or spherical morphologies are obtained. A preliminary screening of the complexes, **13-18** for their antibacterial activity against Gram-positive bacteria, Bacillus *subtilis* reveal that the colloidal particles show antibacterial activity while no inhibition zone was observed for their bulk counterparts.

The work embodies in this chapter also includes spectral studies of diorganotin bis(hydrogenphosphonate)s, $R_2Sn\{OP(O)(OH)CH_2SiMe_3\}_2$ [R = Et (**22**), *n*-Bu (**23**)] and $R_2Sn\{OP(O)(OH)(CH_2)_3SiR^1R^2{}_2\}_2$ [$R^1$, $R^2$ = Et (**24**, **25**); $R^1$ = Ph, $R^2$ = Me (**26**, **27**)] in solution. Based on multinuclear NMR studies, it has been suggested that these compounds adopt a dimeric structure bearing bridging and terminal hydrogenphosphonate groups. The results emerging from these studies are included in chapter IV.

The content of chapter V provides an insight into the reactivity studies of diethyl trimethylsilylmethylphosphonate $Me_3SiCH_2P(O)(OEt)_2$ (**1a**) and its implications in organotin chemistry. The chemical transformation of **1a** into $Me_3SiC(CH_3)_2P(O)(OH)_2$ (**$H_2$L**) and the isolation of a few mixed-ligand diorganotin(IV) coordination polymers, $R_2Sn(HL)(OSO_2Me)$ [R = Me (**29**), *n*-Bu (**31**)] and $(Et_2Sn)_6(L)_4(OSO_2Me)_4$ (**30**) are discussed in this section. These compounds have been characterized by IR, multinuclear NMR as well as X-ray crystal structure analysis (for **30**). The isolation of $MeP(O)(OEt)O^-Na^+$ (**32**) is achieved from the reaction of **1a** with ethanolic sodium hydroxide under optimized conditions. Using this ligand, a few diorganotin bis(*O*-ethylmethylphosphonate)s $R_2Sn\{OP(O)(OEt)Me\}_2$ [R = Me (**33**), Et (**34**), *n*-Bu (**35**)] have been isolated and characterized by spectroscopic methods as well as X-ray crystal structure analysis of **35**. We also examined the reactivity of **1a** towards diorganotin oxides in the presence of triethylamine. This approach has been useful to synthesize α-functionally substituted tetraorganotin compounds, $R_2Sn\{CH_2P(O)(OEt)_2\}_2$ [R = Me (**36**), Et (**37**), *n*-Bu (**38**)]. A putative mechanism for the formation of these compounds has been proposed by considering phosphonate-stabilized carbanion, $(EtO)_2P(O)CH_2^-$ as the intermediate.

# LIST OF FIGURES

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# Glossary of Symbols and Abbreviations

| | |
|---|---|
| % | percent |
| ° | degree |
| °C | degree centigrade |
| Å | Angstrom |
| AFM | atomic force microscopy |
| ATR | attenuated total reflectance |
| br | broad signal |
| b.p. | boiling point |
| d | Doublet |
| D | dimensional |
| ε | molar absorptivity |
| eq. | Equation |
| ESI | electrospray ionization |
| Et | ethyl |
| FT | fourier transform |
| g | gram |
| h | hour |
| HR-TEM | High resolution transmission electron microscopy |
| Hz | hertz |
| ICP | infinite coordination polymer |
| IR | infrared |
| J | coupling constant |
| λ | wavelength |
| μ | micro |

| | |
|---|---|
| m | multiplet |
| m.p. | melting point |
| Me | methyl |
| MHz | mega hertz |
| mL | milliliter |
| mmol | millimole |
| MOF | metal organic framework |
| *n*-Bu | *n*-butyl |
| nm | nanometer |
| NMR | nuclear magnetic resonance |
| ORTEP | Oak Ridge Thermal Ellipsoid Plot |
| Ph | phenyl |
| q | quartet |
| rt | room temperature |
| SEM | scanning electron microscopy |
| t | triplet |
| *t*-Bu | *t*-butyl |
| TGA | thermogravimetric analysis |
| TMS | tetrametylsilane |
| δ | chemical shift |
| ν | frequency |