

**SYNTHESIS AND STRUCTURAL STUDIES OF Sn(IV),
Mg(II) AND Zn(II) COORDINATION POLYMERS
DERIVED FROM PHOSPHONATE/ PHOSPHITE
ESTERS**

SWATI MENDIRATTA



**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
DECEMBER 2017**

© Indian Institute of Technology (IITD), New Delhi, 2017

**SYNTHESIS AND STRUCTURAL STUDIES OF Sn(IV),
Mg(II) AND Zn(II) COORDINATION POLYMERS
DERIVED FROM PHOSPHONATE/ PHOSPHITE
ESTERS**

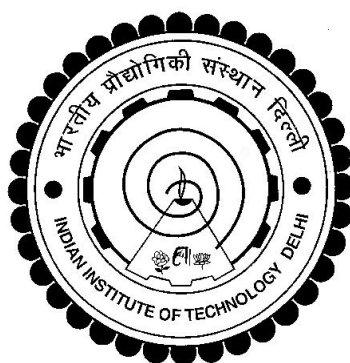
By

SWATI MENDIRATTA

Submitted

In fulfillment of the requirements of the degree of
DOCTOR OF PHILOSOPHY

to the



**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
DECEMBER 2017**

Dedicated to My Family

CERTIFICATE

This is to certify that the thesis entitled “**Synthesis and structural studies of Sn(IV), Mg(II) and Zn(II) coordination polymers derived from phosphonate/ phosphite esters**” being submitted by **Ms. Swati Mendiratta** 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.

She 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.

Prof. Ravi Shankar

Department of Chemistry,
Indian Institute of Technology Delhi,
New Delhi-110016, India

ACKNOWLEDGEMENTS

First and foremost, I would like to thank God Almighty for giving me the strength, knowledge, ability and opportunity to undertake this research study and to persevere and complete it satisfactorily. Without his blessings, this achievement would not have been possible.

This thesis is the result of almost five years of work whereby I have been accompanied and supported by many people. It is a pleasure that I now have the opportunity to express my gratitude to all of them.

I wish to express my deep and sincere gratitude to my supervisor, Prof. Ravi Shankar, Department of Chemistry, Indian Institute of Technology, Delhi for his painstaking guidance and invaluable suggestions. The completion of this project would not have been possible without his active involvement during all stages from the conception to the actual culmination of this project.

In addition, special thanks to the present and erstwhile Heads of Department Prof. Ravi Shankar and Prof. A. Ramanan for providing the necessary facilities for carrying out my research work.

The staff of the Instrumentation Laboratory of Chemistry Department also deserves a special mention. I would like to thank Mr. Keshav and Mr. Alok for recording the NMR data reported in this thesis.

In addition, thanks to Prof. Kieran C. Molloy, Gabriele K.-Köhn (Department of Chemistry, University of Bath, UK) and Prof. K. Jurkschat (Technische Universität Dortmund, Anorganische Chemie) for their help in single crystal X-crystallography. I also thank Dr. Pavletta Shestakova (Bulgarian Academy of sciences, Institute of Organic Chemistry with centre of Phytochemistry) for solid state NMR studies. A special thank to Prof. G. V. Prakash and Mr. Pawan (Department of Physics, IIT Delhi) for their help in Solid state- fluorescence studies.

I would also like to thank UGC CSIR-INDIA for the award of the Junior Research and Senior Research Fellowships, which have supported me during my five years of research.

My extended gratitude to my seniors Dr. Meenal, Dr. Manchal, Dr. Nisha, Dr. Amanpreet Kaur and Rohit Sir for all the encouragements and practical advices, I have received during my Ph.D work. I also wish to express my appreciation and warm feelings to my lab mates, Ekta, Nidhi, Archismati, Nivedita, Prashant, Mohit, Rajinder, Anmol, Vineeta, Jitender, Madhushree and Priya. They have always very supportive, friendly and eager to help.

I wish to express my deep sense of gratitude towards my colleagues Bhawana, Asmita and Nidhi for their love, care and moral support. They were always beside me during the happy and hard moments to push me and motivate me. I have spent some of the best moments of my life with them and can never forget the love, valuable help and support they have provided during my stay in IIT Delhi.

I am extremely grateful to my respectable parents (Mr. Raj Kumar Mendiratta & Mrs. Seema Mendiratta) for their love, prayers, care and sacrifices for educating and preparing me for my future. I owe everything to them. Without their unconditional love, encouragement and continuous support, it would have been impossible for me to arrive where I am today. I would like to thank my brother Bharat for love, patience, motivation and invaluable support that he has always shown for me.

SWATI MENDIRATTA

ABSTRACT

The work presented in the thesis is a systematic study to explore the reactivity of Sn, Zn and Mg metals with organophosphonic acid dialkylesters, $\text{RP}(\text{O})(\text{OR})_2$. The study offers a simple and attractive approach to the formation of coordination assemblies bearing phosphonate ester ligands.

The content of the thesis is divided into five chapters. Chapter I deals with a brief survey of literature highlighting recent advances on the synthesis and structural aspects of metal organic frameworks/infinite coordination polymers with emphasis on organotin compounds and their applications. Chapter II includes detailed description of synthetic methods and analytical techniques for the characterization of new compounds.

A detailed account on the reactivity of elemental tin with organophosphonic acid dialkylesters, $\text{R}^1\text{P}(\text{O})(\text{OR})_2$ is presented in chapter III. A facile reactivity of tin (powder) with $\text{MeP}(\text{O})(\text{OMe})_2$ at elevated temperature ($130\text{ }^\circ\text{C}$) has offered an interesting route to $\text{Me}_2\text{Sn}\{\text{OP}(\text{O})(\text{OMe})\text{Me}\}_2$ *via* concomitant formation of Sn-C and Sn-O(P) bonds. On the contrary, analogous reactions with higher phosphonate diesters, ($\text{R}^1 = \text{OEt}$, OPr^i) essentially require the use of KI as the catalyst to facilitate the formation of diorganotin bis(*O*-alkyl organophosphonate), $\text{R}^1_2\text{Sn}\{\text{OP}(\text{O})(\text{OR})\text{R}^1\}_2$ ($\text{R} = \text{Et}$; $\text{R}^1 = \text{Me}$, Et , allyl, 2-thienyl, benzyl). A plausible mechanistic rationale for the formation of these compounds using tin metal as the precursor has been put forth. The key steps in the proposed catalytic cycle involve the formation of $\text{R}^1\text{P}(\text{O})(\text{OEt})\text{O}^-\text{K}^+$ *via* mono-dealkylation of the phosphonate diester and *in situ* generation of alkyl iodide, RI. Subsequent reaction of the metal with alkyl iodide affords the formation of RSnI or R_2SnI_2 as the reactive intermediate. All the compounds thus synthesized have been characterized by routine spectroscopy as well as single crystal X-ray

crystallography. All the compounds are isostructural and adopt one-dimensional motif by virtue of bridging bidentate character of the phosphonate monoester ligand. The scope of these preformed coordination polymers as synthetic precursors has been elucidated by the isolation of a tin(II) phosphonate, $\text{Sn}\{\text{O}_2\text{P}(\text{OH})\text{Me}\}_2 \cdot 4,4'\text{-bipy}$ from the reaction of $\text{Me}_2\text{Sn}\{\text{OP}(\text{O})(\text{OMe})\text{Me}\}_2$ with 4,4'-bipyridine under reflux conditions (H_2O - EtOH , 120 °C, 3 days). A detailed mechanism of the formation of Sn(II) assembly *via* cleavage of Sn-Me bonds is yet to be clearly understood. The reactivity of tin powder with dialkylphosphites, $\text{HP}(\text{O})(\text{OR})_2$ has also been examined and led to the development of a new method for the synthesis of diorganotin bis(*O*-alkyl phosphite)s, $\text{R}_2\text{Sn}\{\text{OP}(\text{O})(\text{OR})\text{H}\}_2$ ($\text{R} = \text{Me}, \text{Et}$).

The content of chapter IV deals with the reactions of elemental zinc with organophosphonic acid dialkylesters, $\text{R}^1\text{P}(\text{O})(\text{OR})_2$ under conditions similar to those described in chapter III. A series of zinc-phosphonate esters, $\text{Zn}\{\text{OP}(\text{O})(\text{OR})\text{R}^1\}_2$ [$\text{R} = \text{R}^1 = \text{Me}, \text{Et}$; $\text{R} = \text{Et}, \text{R}^1 = \text{benzyl}, \text{allyl}$] have been isolated by following this approach. The catalytic role of KI has been demonstrated in promoting these reactions as well. X-ray crystallographic study of $\text{Zn}\{\text{OP}(\text{O})(\text{OMe})\text{Me}\}_2$ reveals that the structure adopts a one-dimensional polymeric motif featuring an infinite array of vertex shared eight membered $[-\text{Zn}-\text{O}-\text{P}-\text{O}-]_2$ cyclic rings. The preformed polymer reacts with 4,4'-bipyridine (4, 4'-bipy) or 1, 2-bis(4-pyridyl)ethane (1, 2-bpe) under hydrothermal conditions (140-150 °C, 3 days) to afford the formation of $\{\text{Zn}(\text{O}_3\text{PMe})(4,4'\text{-bipy})_{0.5}\} \cdot 2\text{H}_2\text{O}$ and $\{\text{Zn}(\text{O}_3\text{PMe})(1,2\text{-bpe})_{0.5}\} \cdot \text{H}_2\text{O}$. Based on crystallographic studies, the structural motifs of these compounds featuring ladder like zinc-phosphonate framework are unequivocally established. The N-donor ligands assist the formation of a layered structure in each case. The reactivity of Mg finds a close analogy with that of Zn as evident from the isolation of magnesium bis(*O*-alkyl organophosphonate), $\text{Mg}\{\text{OP}(\text{O})(\text{OR})\text{R}^1\}_2$. On the other hand, similar reactions of Mg with phosphite diesters,

HP(O)(OR)₂ (R = Me, Et) have led to the isolation of a mixture of products composed of Mg{OP(O)(OR)H}₂ and Mg{OP(O)(OR)R}₂ [R = Me, Et], suggesting partial alkylation of P-H bonds during the reaction. Transesterification reaction of Mg{OP(O)(OEt)H}₂ (**A**) and Mg{OP(O)(OEt)Et}₂ (**B**) with methanol reveals that the transformation of P-OEt to P-OMe in coordinated phosphite (**A**) is quite facile while the phosphonate moiety in **B** remains inert.

The content of chapter V deals with synthesis and structural studies of triorganotin *O*-alkyl organophosphonates, R₃SnOP(O)(OR¹)R¹ (R = Me, *n*-Bu, Ph, Bn; R¹ = Me, Et). These compounds are easily accessible by reacting an appropriate triorganotin chloride with the organophosphonic acid dialkyl esters. X-ray crystallographic studies reveal that these compounds are isostructural and adopt one dimensional polymeric motif with trigonal bipyramidal geometry at tin center. In the later part of this chapter, a generic method, which involves the reactivity of Me₃SiCH₂P(O)(OEt)₂ with bis(triorganotin)oxide, has been developed for the synthesis of α -functionally substituted tetraorganotin compounds, R₃SnCH₂P(O)(OEt)₂ (R = Ph, *n*-Bu, Bn). A plausible mechanism involving *in situ* generation of phosphonate-stabilized carbanion as the reactive intermediate has been proposed. The reactions of Ph₃SnCH₂P(O)(OEt)₂ with X₂ (X = Br, I) under optimized conditions allowed the synthesis of new functional tetraorganotin compounds, Ph_{3-n}(X)_nSnCH₂P(O)(OEt)₂ (n = 1 or 2, X = Br, I). X-ray crystallographic studies reveal that these compounds adopt a dimeric structure by virtue of two intermolecular P=O→Sn interactions.

विषय सार

शोध प्रबंध में प्रस्तुत कार्य Sn, Zn और Mg धातुओं की उत्प्रेरण ऑर्गनोफ़ॉस्फ़ोनिक एसिड डीअल्काइल एस्टर्स, $RP(O)(OR)_2$ के साथ करने के लिए एक व्यवस्थित अध्ययन है। यह अध्ययन फोस्फोनेट एस्टर्स लिगेंड के समन्वित संयोजन के गठन के लिए एक सरल और आकर्षक दृष्टिकोण प्रदान करता है।

शोध प्रबंध को पांच अध्यायों में विभाजित किया गया है। अध्याय I साहित्य के संक्षिप्त सर्वेक्षण से संबंधित धातु कार्बनिक फ्रेमवर्क/ अनंत समन्वय पॉलिमर के संश्लेषण और संरचनात्मक पहलुओं पर आधुनिक प्रगति को उजागर करता है जो ऑर्गनोटिन यौगिकों और उनके अनुप्रयोगों पर जोर देते हैं। अध्याय II में नए यौगिकों के लक्षण वर्णन के लिए कृत्रिम प्रक्रियाओं और विश्लेषणात्मक तकनीकों का विस्तृत वर्णन शामिल है।

अध्याय III में ऑर्गनोफ़ॉस्फ़ोनिक एसिड डीअल्काइल एस्टर्स, $R^1P(O)(OR)_2$ के साथ मौलिक टिन की प्रक्रिया पर एक विस्तृत विवरण प्रस्तुत किया गया है। टिन पाउडर की सहज प्रक्रिया $MeP(O)(OMe)_2$ के साथ उच्च तापमान ($130\text{ }^{\circ}C$) पर, $Sn-C$ $Sn-O(P)$ बांड के सहवर्ती गठन के माध्यम से $Me_2Sn\{OP(O)(OMe)Me\}_2$ के निर्माण के लिए एक दिलचस्प मार्ग प्रदान करती है। इसके विपरीत, उच्च फ़ॉस्फ़ोनेट डीअल्काइल एस्टर्स, $(R = Et, Pr^i)$ के साथ समान रूप से प्रक्रियाओं को डाईऑर्गनोटिन बिस(ओ-अल्काइल ऑर्गनोफ़ॉस्फ़ोनेट)स, $R^1_2Sn\{OP(O)(OR)R^1\}_2$ ($R = Et$; $R^1 = Me, Et, allyl, 2-thienyl, benzyl$) के गठन की सुविधा के लिए अनिवार्य रूप से उत्प्रेरक के रूप में KI के उपयोग की आवश्यकता होती है। इन यौगिकों के निर्माण के लिए एक सुव्यवस्थित यंत्रवत तर्क अग्रगण्य के रूप में टिन धातु का इस्तेमाल किया गया है। प्रस्तावित उत्प्रेरक चक्र के महत्वपूर्ण कदमों में फ़ॉस्फ़ोनेट डीएस्टर्स की मोनोडिल्किलेशन के माध्यम से $R^1P(O)(OEt)O^{\cdot-}K^+$ के गठन और अल्काइल आयोडाइड, RI की उत्पत्ति शामिल है। अल्काइल आयोडाइड के साथ टिन की अनुवर्ती

प्रक्रिया रिएक्टिव इंटरमीडिएट के रूप में R_2SnI या R_2SnI_2 का गठन करती है। इस प्रकार संश्लेषित सभी यौगिकों को नियमित स्पेक्ट्रोस्कोपी और सिंगल क्रिस्टल X-ray क्रिस्टलोग्राफी द्वारा चिह्नित किया गया है। सभी यौगिक फ़ॉस्फ़ोनेट मोनोएस्टर लिगेंड ब्रिजिंग बिंडेट के चरित्र के आधार पर आइसोस्ट्रक्चरल और एक आयामी आकृति को अपनाते हैं। इन समन्वित पॉलीमर, $Me_2Sn\{OP(O)(OMe)Me\}_2$ को कृत्रिम अग्रदूत के रूप में जांचा गया और 4,4'-बायिपिरिडिन (4,4'-bipy) की प्रक्रिया ($H_2O-EtOH$, $120^\circ C$, 3 दिन) से एक नया पॉलीमर, $Sn\{O_2P(OH)Me\}_2 \cdot 4,4'-bipy$ प्राप्त हुआ। $Sn-Me$ के टूटने के माध्यम से $Sn(II)$ संयोजन के गठन का एक विस्तृत तंत्र अभी स्पष्ट रूप से समझ नहीं आया है। डीअल्काइल फ़ॉस्फ़िट, $HP(O)(OR)_2$ के साथ टिन पाउडर की प्रक्रिया की भी जांच की गई है और डाईऑर्गनोटिन बिस (ओ-अल्काइल फ़ॉस्फ़िट)स, $R_2Sn\{OP(O)(OR)H\}_2$ ($R = Me, Et$) के संश्लेषण के लिए एक नई विधि दर्शाई गई है।

अध्याय IV, ऑर्गनोफ़ॉस्फ़ोनिक एसिड डीअल्काइल एस्टर्स, $R^1P(O)(OR)_2$ के साथ मैटेलिक Zn की प्रक्रियाओं से संबंधित है जो अध्याय III में Sn धातु के लिए भी समान रूप से वर्णित किया गया है। इस दृष्टिकोण का अनुसरण करके Zn - फ़ॉस्फ़ोनेट एस्टर्स की श्रृंखला, $Zn\{OP(O)(OR)R^1\}_2$ [$R = R^1 = Me, Et$; $R = Et, R^1 = benzyl, allyl$] को बनाया गया है। KI का उत्प्रेरक भूमिका इन प्रक्रियाओं को भी बढ़ावा देने में दिखाई गई है। क्रिस्टलोग्राफिक अध्ययन से पता चलता है कि $Zn\{OP(O)(OMe)Me\}_2$ की संरचना एक आयामी पॉलीमरिक आकृति को अपनाता है जिसमें असीमित सारिणी की संख्या को अष्ट सदस्यी $[-Zn-O-P-O-]_2$ चक्रीय रिंगों के साथ साझा किया गया है। 4,4'-बायिपिरिडिन (4, 4'-bipy) और 1, 2- बिस(4- प्यरीडील ईथेन) (1, 2-bpe) के साथ जलतापीय शर्तों ($140-150^\circ C$, 3 दिन) में पूर्वनिर्मित बहुलक, $Zn\{OP(O)(OMe)Me\}_2$ की प्रक्रिया के नतीजे से $\{Zn(O_3PMe)(4,4'-bipy)_{0.5}\} \cdot 2H_2O$ और $\{Zn(O_3PMe)(1,2-bpe)_{0.5}\} \cdot H_2O$ का निर्माण होता है। क्रिस्टलोग्राफिक अध्ययन के आधार पर इन यौगिकों के संरचनात्मक रूपांकनों में Zn - फोस्फोनेट का ढांचा एक सीढ़ी की तरह स्पष्ट रूप से स्थापित है। N- दाता सपहंदके प्रत्येक मामले में एक स्तरित संरचना के गठन की सहायता

करते हैं। Mg- बिस(ओ-अल्काइल ऑर्गनोफ़ॉस्फ़ोनेट)स, $Mg\{OP(O)(OR)R^1\}_2$ का विशिष्ट निर्माण स्पष्ट रूप से Mg और Zn समान प्रक्रिया को दर्शाता है। दूसरी ओर Mg की फ़ॉस्फ़िट डीअल्काइल एस्टर्स, $HP(O)(OR)_2$ ($R = Me, Et$) के साथ समान प्रक्रियाओं से बने $Mg\{OP(O)(OR)H\}_2$ और $Mg\{OP(O)(OR)R\}_2$ [$R = Me, Et$] का मिश्रित उत्पाद प्रक्रिया के दौरान P-H बंधों के आंशिक अल्केलिटिंग का सुझाव देता है। $Mg\{OP(O)(OEt)H\}_2$ (**A**) and $Mg\{OP(O)(OEt)Et\}_2$ (**B**) के मेथनॉल (MeOH) के साथ ट्रांसएस्टेरिफिकेशन प्रक्रिया से पता चलता है कि P-OEt को P-OMe का परिवर्तन करने में समन्वित फ़ॉस्फ़िट (**A**) काफी सहज है जबकि **B** का फ़ॉस्फ़ोनेट भाग निष्क्रिय रहता है।

अध्याय V ट्राईऑर्गनोटिन फ़ॉस्फ़ोनेट, $R_3SnOP(O)(OR^1)R^1$ ($R = Me, n-Bu, Ph, Bn$; $R^1 = Me, Et$) की कृत्रिम रचना और संरचनात्मक अध्ययन से संबंधित है। ये यौगिक ऑर्गनोफोस्फ़ोनीक एसिड डीअल्काइल एस्टर की उपयुक्त ट्राईऑर्गनोटिन क्लोराइड के साथ प्रक्रिया करने पर सुलभता से प्राप्त होते हैं। X-ray क्रिस्टलोग्राफ़िक अध्ययन से पता चलता है कि ये योगिकाएँ ईसोस्ट्रक्चरल हैं और टिन सेंटर, ट्रिगोनल बिपरयामिडल ज्यामिति के साथ एक आयामी बहुलक आकृति को दर्शाता है। इस अध्याय के दूसरे भाग में एक सामान्य पद्धति है, जिसमें बिस (ट्राईऑर्गनोटिन) ऑक्साइड के साथ $Me_3SiCH_2P(O)(OEt)_2$ की प्रक्रिया को शामिल करते हुए कार्यात्मक रूप से α -प्रतिस्थापित टेट्राऑर्गनोटिन यौगिकों, $R_3SnCH_2P(O)(OEt)_2$ ($R = Ph, n-Bu, Bn$) के संश्लेषण के लिए विकसित किया गया है। प्रक्रियाशील मध्यवर्ती के रूप में फ़ॉस्फ़ोनेट स्थायी कार्बोनायन के तत्रस्थ उत्पादन के लिए एक सुव्यवस्थित तंत्र प्रस्तावित किया गया है। अनुकूलित परिस्थितियों में $Ph_3SnCH_2P(O)(OEt)_2$ के साथ X_2 ($X = Br, I$) की प्रक्रियाओं ने नए फंक्शनल टेट्राऑर्गनोटिन यौगिकों, $Ph_{3-n}(X)_nSnCH_2P(O)(OEt)_2$ ($n = 1 \text{ or } 2, X = Br, I$) के संश्लेषण की अनुमति दी है। X-ray क्रिस्टलोग्राफ़िक अध्ययन से पता चलता है कि ये यौगिक दो अंतःक्रियात्मक $P=O \rightarrow Sn$ इंटरैक्शन के आधार पर एक डायमेरिक संरचना को अपनाते हैं।

CONTENTS

	Page No.
Abstract	i
List of Figures	iv
List of Tables	vii
Glossary of Symbols and Abbreviations	xi
CHAPTER I Introduction	1-14
Scope and aim	15-16
CHAPTER II Materials and methods	17-34
CHAPTER III Reactions of elemental tin with organophosphonic acid dialkylesters/ H-phosphonic acid dialkylesters: Synthesis and characterization of diorganotin bis(<i>O</i> -alkylorganophosphonate)s/ diorganotin bis(<i>O</i> -alkylphosphite)s	35-59
CHAPTER IV Reactions of elemental zinc and magnesium with organophosphonic acid dialkylesters/ H-phosphonic acid dialkylesters	60-84
CHAPTER V Synthesis and characterization of triorganotin <i>O</i> -alkyl organophosphonates and α -functionally substituted tetraorganotin compounds	85-110
REFERENCES	111-125
APPENDIX Figures and Tables	126-149

BIODATA OF THE AUTHOR

LIST OF FIGURES

Figure No.	Description	Page No.
Chapter III		
3.1	(a) ^1H and (b) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Me}_2\text{Sn}\{\text{OP}(\text{O})(\text{OMe})\text{Me}\}_2$ (1).	37
3.2	^1H NMR spectrum of $\text{Et}_2\text{Sn}\{\text{OP}(\text{O})(\text{OEt})\text{allyl}\}_2$ (4)	42
3.3	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Et}_2\text{Sn}\{\text{OP}(\text{O})(\text{OEt})\text{Me}\}_2$ (2).	42
3.4	$^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of $\text{Et}_2\text{Sn}\{\text{OP}(\text{O})(\text{OEt})2\text{-Th}\}_2$ (5) in solid state.	43
3.5	(a) A perspective view of molecular structure of $\text{Et}_2\text{Sn}\{\text{OP}(\text{O})(\text{OEt})\text{Me}\}_2$ (2). Thermal ellipsoids are set at 50 % probability. (b) 1D structure of 2 . All hydrogen atoms are omitted for clarity.	45
3.6	Structure of $\text{Et}_2\text{Sn}\{\text{OP}(\text{O})(\text{OEt})2\text{-Th}\}_2$ (5) showing atom connectivity.	46
3.7	(a) A perspective view of molecular structure of $\text{Me}_2\text{Sn}\{\text{OP}(\text{O})(\text{OPr}^i)\text{Me}\}_2$ (7). Thermal ellipsoids are set at 50 % probability. (b) 1D structure of 7 . All hydrogen atoms are omitted for clarity.	50
3.8	$^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of (a) $\text{Sn}\{\text{O}_2\text{P}(\text{OH})\text{Me}\}_2\cdot 4,4'\text{-bipy}$ (8) and (b) $\text{Me}_2\text{Sn}\{\text{OP}(\text{O})(\text{OMe})\text{Me}\}_2$ (1).	52
3.9	(a) A perspective view of 1D structure of $\text{Sn}\{\text{O}_2\text{P}(\text{OH})\text{Me}\}_2\cdot 4,4'\text{-bipy}$ (8). (b) Layered structure of 8 . All hydrogen atoms except in P-OH groups are omitted for clarity.	54
3.10	^1H NMR spectrum of $\text{Et}_2\text{Sn}\{\text{OP}(\text{O})(\text{OEt})\text{H}\}_2$ (10).	57
3.11	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Me}_2\text{Sn}\{\text{OP}(\text{O})(\text{OMe})\text{H}\}_2$ (9).	57
Chapter IV		
4.1	A perspective view of molecular structure of $\text{Zn}\{\text{OP}(\text{O})(\text{OMe})\text{Me}\}_2$ (11). Thermal ellipsoids are set at 50% probability. (b) 1D structure of 11 . All hydrogen atoms are omitted for clarity.	66
4.2	(a) Building unit of $\{\text{Zn}(\text{O}_3\text{PMe})(4,4'\text{-bipy})_{0.5}\}\cdot 2\text{H}_2\text{O}$ (15) in	71

Figure No.	Description	Page No.
	ORTEP view. Thermal ellipsoids are set at 50 % probability. A perspective view showing (b) layered motif (water molecules and all hydrogen atoms are omitted for clarity), (c) 3D structure and (d) 1D array of water assembly.	
4.3	(a) Building unit of $\{Zn(O_3PMe)(1,2-bpe)_{0.5}\} \cdot H_2O$ (16) in ORTEP view. Thermal ellipsoids are set at 50 % probability. (b) A perspective view showing layered motif. Dashed lines (in blue) represent O-H $\cdots$ O hydrogen bonds.	72
4.4	(a) 1H and (b) $^{31}P\{^1H\}$ NMR spectrum of a mixture of $Mg\{OP(O)(OMe)H\}_2$ and $Mg\{OP(O)(OMe)Me\}_2$ (21).	78
4.5	(a) 1H and (b) $^{31}P\{^1H\}$ NMR spectrum of a mixture of $Mg\{OP(O)(OEt)H\}_2$ and $Mg\{OP(O)(OEt)Et\}_2$ (22).	79
4.6	1H NMR spectra showing transesterification of (22) with methanol at different time intervals (chemical shift region at δ 4.8 corresponds to residual peak due to D_2O).	82
Chapter V		
5.1	$^{13}C\{^1H\}$ NMR spectrum of $Me_3SnOP(O)(OMe)Me$ (24).	90
5.2	$^{13}C\{^1H\}$ NMR spectrum of $n-Bu_3SnOP(O)(OMe)Me$ (25).	90
5.3	(a) $^{119}Sn\{^1H\}$ and (b) $^{31}P\{^1H\}$ NMR spectrum of $Ph_3SnOP(O)(OEt)Et$ (29).	92
5.4	(a) ORTEP view of asymmetric unit of $Me_3SnOP(O)(OMe)Me$ (24). Thermal ellipsoids are set at 30 % probability. (b) 1D structure of 24 . All hydrogen atoms are omitted for clarity.	93
5.5	ORTEP view of asymmetric unit of $Bn_3SnOP(O)(OMe)Me$ (26). Thermal ellipsoids are set at 30 % probability. (b) 1D structure of 26 . All hydrogen atoms are omitted for clarity.	95
5.6	(a) ORTEP view of asymmetric unit of $Ph_3SnOP(O)(OEt)Et$ (29). Thermal ellipsoids are set at 30 % probability. (b) 1D structure of 29 . All hydrogen atoms are omitted for clarity.	97
5.7	Crystal structure of $Ph_3SnCl \cdot L$ [$L = BnP(O)(OEt)_2$] (31). All	98

Figure No.	Description	Page No.
	hydrogen atoms are omitted for clarity.	
5.8	$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of (a) $\text{Me}_3\text{SiCH}_2\text{P}(\text{O})(\text{OEt})_2$, (b) reaction mixture and (c) product (32).	101
5.9	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Ph}_3\text{SnCH}_2\text{P}(\text{O})(\text{OEt})_2$ (32).	105
5.10	(a) $^{31}\text{P}\{^1\text{H}\}$ and (b) $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of <i>n</i> - $\text{Bu}_3\text{SnCH}_2\text{P}(\text{O})(\text{OEt})_2$ (33).	105
5.11	ORTEP view of crystal structures of (a) $\text{Ph}_2(\text{Br})\text{SnCH}_2\text{P}(\text{O})(\text{OEt})_2$ (35). (b) $\text{Ph}_2(\text{I})\text{SnCH}_2\text{P}(\text{O})(\text{OEt})_2$ (36) and (c) $\text{Ph}(\text{Br})_2\text{SnCH}_2\text{P}(\text{O})(\text{OEt})_2$ (37). Thermal ellipsoids are set at 30% probability. All hydrogen atoms are omitted for clarity.	107
5.12	ESI-MS of $\text{Ph}_2(\text{Br})\text{SnCH}_2\text{P}(\text{O})(\text{OEt})_2$ (35) and its hydrolysis products.	109
	Appendix	
A1	Thermogravimetric analysis (TGA) of $\text{R}_2\text{Sn}\{\text{OP}(\text{O})(\text{OR})\text{R}^1\}_2$ 2-6.	129
A2	Thermogravimetric analysis of $\text{Zn}\{\text{OP}(\text{O})(\text{OR})\text{R}^1\}_2$ [$\text{R} = \text{R}^1 = \text{Me}$ (11); $\text{R} = \text{Et}$, $\text{R}^1 = \text{Bn}$ (13), allyl (14)].	133
A3	Powder X-ray diffraction pattern of $\text{Zn}\{\text{OP}(\text{O})(\text{OMe})\text{Me}\}_2$ (11) (a) simulated, (b) as-synthesized and (c) upon water exposure for 5-7 days.	133
A4	^1H and (b) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Zn}\{\text{OP}(\text{O})(\text{OMe})\text{Me}\}_2$ (11).	134
A5	^1H NMR spectrum of $\text{Zn}\{\text{OP}(\text{O})(\text{OEt})\text{Et}\}_2$ (12).	135
A6	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Zn}\{\text{OP}(\text{O})(\text{OEt})\text{Bn}\}_2$ (13).	135
A7	A comparison of ATR-IR spectra of $\text{Zn}\{\text{OP}(\text{O})(\text{OMe})\text{Me}\}_2$ (11) and $\{\text{Zn}(\text{O}_3\text{PMe})(4,4'\text{-bipy})_{0.5}\} \cdot 2\text{H}_2\text{O}$ (15).	136
A8	Thermogravimetric analysis of $\{\text{Zn}(\text{O}_3\text{PMe})(4,4'\text{-bipy})_{0.5}\} \cdot 2\text{H}_2\text{O}$ (15) and $\{\text{Zn}(\text{O}_3\text{PMe})(1,2\text{-bpe})_{0.5}\} \cdot \text{H}_2\text{O}$ (16).	137
A9	X-ray powder diffraction pattern of $\{\text{Zn}(\text{O}_3\text{PMe})(4,4'\text{-bipy})_{0.5}\} \cdot 2\text{H}_2\text{O}$ (15) after pyrolysis at 600 °C and the JCPDS data for $\text{Zn}_2\text{P}_2\text{O}_7$	137

Figure No.	Description	Page No.
A10	Solid state fluorescence spectra of (a) $\{Zn(O_3PMe)(4,4'-bipy)_{0.5}\} \cdot 2H_2O$ (15) and (b) $\{Zn(O_3PMe)(1,2-bpe)_{0.5}\} \cdot H_2O$ (16).	138
A11	Thermogravimetric analysis (TGA) of $Mg\{OP(O)(OR)R^1\}_2$ [$R = R^1 = Me$ (17), $R^1 = Et$, $R = Bn$ (19), allyl (20)].	139
A12	$^{31}P\{^1H\}$ NMR spectrum of reaction mixture of $Mg\{OP(O)(OMe)H\}_2$ (A) and $Mg\{OP(O)(OMe)Me\}_2$ (B) (21).	139
A13	Thermogravimetric analysis (TGA) of $R_3SnOP(O)(OR^1)R^1$ [$R^1 = Me$, $R = Me$ (24), Bn (26); $R^1 = Et$, $R = Ph$ (29), Bn (30)].	145
A14	ESI-MS of thermolysis product of $Ph_3SnCl \cdot BnP(O)(OEt)_2$ (31). M' represents $Ph_3SnOP(O)(OEt)Bn$.	145

LIST OF TABLES

Table No.	Description	Page No.
Chapter III		
3.1	^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectral data (δ , J) of $\text{R}_2\text{Sn}\{\text{O}(\text{P})(\text{O})(\text{OR})\text{R}^1\}_2$ [$\text{R} = \text{R}^1 = \text{Me}$ (1); $\text{R} = \text{Et}$, $\text{R}^1 = \text{Me}$ (2), Et (3), allyl (4), 2-Th (5), Bn (6)], $\text{MeSn}\{\text{OP}(\text{O})(\text{OPr}^i)\text{Me}\}_2$ (7).	40-41
Chapter IV		
4.1	^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectral data (δ , J) of $\text{Zn}\{\text{OP}(\text{O})(\text{OR})\text{R}^1\}_2$ [$\text{R} = \text{R}^1 = \text{Me}$ (11), Et (12); $\text{R} = \text{Et}$, $\text{R}^1 = \text{Bn}$ (13), allyl (14)].	65
4.2	^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectral data (δ , J) of $\text{Mg}\{\text{OP}(\text{O})(\text{OR})\text{R}^1\}_2$ [$\text{R} = \text{R}^1 = \text{Me}$ (17), Et (18); $\text{R} = \text{Et}$, $\text{R}^1 = \text{Bn}$ (19), allyl (20)] and $[\text{Mg}\{\text{OP}(\text{O})(\text{OR})\text{H}\}_2 + \text{Mg}\{\text{OP}(\text{O})(\text{OR})\text{R}\}_2]$ [$\text{R} = \text{Me}$ (21), Et (22)].	77
Chapter V		
5.1	^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectral data (δ , J) of $\text{R}_3\text{SnOP}(\text{O})(\text{OR}^1)\text{R}^1$ [$\text{R}^1 = \text{Me}$, $\text{R} = \text{Me}$ (24), $n\text{-Bu}$ (25), Bn (26); $\text{R}^1 = \text{Et}$, $\text{R} = \text{Me}$ (27), $n\text{-Bu}$ (28), Ph (29), Bn (30)]	88-89
5.2	^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectral data (δ , J) of $\text{R}_3\text{SnCH}_2\text{P}(\text{O})(\text{OEt})_2$ [$\text{R} = \text{Ph}$ (32), $n\text{-Bu}$ (33), Bn (34)].	104
5.3	^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectral data (δ , J) of $\text{Ph}_{3-n}(\text{X})_n\text{SnCH}_2\text{P}(\text{O})(\text{OEt})_2$ [$n = 1$, $\text{X} = \text{Br}$ (35), I (36); $n = 2$, $\text{X} = \text{Br}$ (37), I (38)].	108
Appendix		
A1	Summary of the crystallographic data for $\text{Et}_2\text{Sn}\{\text{OP}(\text{O})(\text{OEt})\text{Me}\}_2$ (2) and $\text{Me}_2\text{Sn}\{\text{OP}(\text{O})(\text{OPr}^i)\text{Me}\}_2$ (7).	125

A2	Selected bond lengths (Å) and bond angles (°) for $\text{Et}_2\text{Sn}\{\text{OP}(\text{O})(\text{OEt})\text{Me}\}_2$ (2).	126
A3	Selected bond lengths (Å) and bond angles (°) for $\text{Me}_2\text{Sn}\{\text{OP}(\text{O})(\text{OPr}^i)\text{Me}\}_2$ (7).	126
A4	Summary of the crystallographic data for $\text{Sn}\{\text{O}_2\text{P}(\text{OH})\text{Me}\}_{2,4,4'}\text{-bipy}$ (8).	127
A5	Selected bond lengths (Å) and bond angles (°) for $\text{Sn}\{\text{O}_2\text{P}(\text{OH})\text{Me}\}_{2,4,4'}\text{-bipy}$ (8).	128
A6	Summary of crystallographic data for $\text{Zn}\{\text{OP}(\text{O})(\text{OMe})\text{Me}\}_2$ (11), $\{\text{Zn}(\text{O}_3\text{PMe})(4,4'\text{-bipy})_{0.5}\} \cdot 2\text{H}_2\text{O}$ (15) and $\{\text{Zn}(\text{O}_3\text{PMe})(1,2\text{-bpe})_{0.5}\} \cdot \text{H}_2\text{O}$ (16).	130
A7	Selected bond lengths (Å) and bond angles (°) for $\text{Zn}\{\text{OP}(\text{O})(\text{OMe})\text{Me}\}_2$ (11).	131
A8	Selected bond lengths (Å) and bond angles (°) for $\{\text{Zn}(\text{O}_3\text{PMe})(4,4'\text{-bipy})_{0.5}\} \cdot 2\text{H}_2\text{O}$ (15).	131
A9	Hydrogen bonds for $\{\text{Zn}(\text{O}_3\text{PMe})(4,4'\text{-bipy})_{0.5}\} \cdot 2\text{H}_2\text{O}$ (15) (Å and °).	132
A10	Selected bond lengths (Å) and bond angles (°) for $\{\text{Zn}(\text{O}_3\text{PMe})(1,2\text{-bpe})_{0.5}\} \cdot \text{H}_2\text{O}$ (16).	132
A11	Hydrogen bonds for $\{\text{Zn}(\text{O}_3\text{PMe})(1,2\text{-bpe})_{0.5}\} \cdot \text{H}_2\text{O}$ (16) (Å and °).	132
A12	Summary of crystallographic data for $\text{Me}_3\text{SnOP}(\text{O})(\text{OMe})\text{Me}$ (24) and $\text{Bn}_3\text{SnOP}(\text{O})(\text{OMe})\text{Me}$ (26).	140
A13	Summary of crystallographic data for $\text{Ph}_3\text{SnOP}(\text{O})(\text{OEt})\text{Et}$ (29) and $\text{Ph}_3\text{SnCl} \cdot \text{L}$ [$\text{L} = \text{BnP}(\text{O})(\text{OEt})_2$] (31).	141
A14	Selected bond lengths (Å) and bond angles (°) for $\text{Me}_3\text{SnOP}(\text{O})(\text{OMe})\text{Me}$ (24).	142
A15	Selected bond lengths (Å) and bond angles (°) for $\text{Bn}_3\text{SnOP}(\text{O})(\text{OMe})\text{Me}$ (26).	142

A16	Selected bond lengths (Å) and bond angles (°) for $\text{Ph}_3\text{SnOP}(\text{O})(\text{OEt})\text{Et}$ (29).	143
A17	Selected bond lengths (Å) and bond angles (°) for $\text{Ph}_3\text{SnCl.L}$ [$\text{L} = \text{BnP}(\text{O})(\text{OEt})_2$] (31).	144
A18	Summary of crystallographic data for $\text{Ph}_3\text{-}$ $\text{n}(\text{X})\text{nSnCH}_2\text{P}(\text{O})(\text{OEt})_2$ [$\text{n} = 1, \text{X} = \text{Br}$ (35), I (36); $\text{n} = 2, \text{X}$ $=\text{Br}$ (37)].	146
A19	Selected bond lengths (Å) and bond angles (°) for $\text{Ph}_2(\text{Br})\text{SnCH}_2\text{P}(\text{O})(\text{OEt})_2$ (35).	147
A20	Selected bond lengths (Å) and bond angles (°) for $\text{Ph}_2(\text{I})\text{SnCH}_2\text{P}(\text{O})(\text{OEt})_2$ (36).	147
A21	Selected bond lengths (Å) and bond angles (°) for $\text{Ph}(\text{Br})_2\text{SnCH}_2\text{P}(\text{O})(\text{OEt})_2$ (37).	148

Glossary of Symbols and Abbreviations

%	percent
°	degree
°C	degree centigrade
Å	Angstrom
ATR	attenuated total reflectance
Bn	Benzyl
br	broad signal
b.p.	boiling point
CH ₂ Cl ₂	dichloromethane
CHCl ₃	chloroform
d	Doublet
D	Dimensional
DMSO	dimethyl sulfoxide
eq.	Equation
ESI	electrospray ionization
Et	ethyl
Et ₂ O	diethyl ether
FT	fourier transform
g	Gram
h	hour
Hz	hertz
ICP	infinite coordination polymer
IR	infrared
<i>J</i>	coupling constant
JCPDS	Joint Committee on Powder Diffraction Standards

λ	wavelength
μ	micro
m	multiplet
m.p.	melting point
Me	methyl
MHz	mega hertz
mL	milliliter
mmol	millimole
MOF	metal organic framework
<i>n</i> -Bu	<i>n</i> -butyl
nm	nanometer
NMR	nuclear magnetic resonance
ORTEP	Oak Ridge Thermal Ellipsoid Plot
Ph	phenyl
<i>i</i> -Pr	<i>iso</i> -propyl
q	quartet
rt	room temperature
Σ	sum
t	triplet
<i>n</i> -Bu	<i>n</i> -butyl
TGA	thermogravimetric analysis
TMS	tetrametylsilane
2-Th	2-thienyl
δ	chemical shift
ν	frequency