SYNTHESIS, CHARACTERIZATION, AND PROTON CONDUCTION BEHAVIOUR OF COORDINATION POLYMERS DERIVED FROM OXY PHOSPHORUS LIGANDS

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by

EKTA JAKHAR

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Dedicated to My Grandmother

CERTIFICATE

This is to certify that the thesis entitled '***SYNTHESIS, CHARACTERIZATION, AND PROTON CONDUCTION BEHAVIOUR OF COORDINATION POLYMERS DERIVED FROM OXY PHOSPHORUS LIGANDS***' being submitted by Ms. Ekta Jakhar 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 the 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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ABSTRACT

The work presented in this thesis is a systematic study to develop a rational synthesis of organoamine mediated zinc phosphite/phosphonate-based coordination assemblies. The use of phosphonate/ phosphite diesters instead of conventional oxy-phosphorus acids in hydro-/solvothermal reactions provides an insight into the genesis of higher dimensional structural motifs *via* the isolation of intermediate phases. Several new organic-inorganic hybrids have been isolated and their proton conduction behaviour studied. The inclusion of imidazole/imidazolium cations in the structural frameworks, such as $[H_2Im]_2[Zn_3(HPO_3)_4]$ and $[Zn(HPO_3)(HIm)]$ offers an intrinsic proton source to enable high proton conductivity on the order of 10^{-3}-10^{-4} S cm^{-1} at 35 and 77% RH in the temperature range of 25-100°C. The synthetic approach has been extended to the zinc phosphonate family. The results are described in chapter III. In chapter IV, new cadmium phosphites, $[Cd\{OP(O)(OH)H\}_2\cdot(4,4'\text{-bipy})]$, $[H_2pip][Cd(O_3PH)\cdot H_2O]\cdot H_2O$ and a mixed ligand coordination polymer, $[Cd(OAc)(ox)_{0.5}(bix)]$ formed by *in situ* formation of oxalate (ox) ligand are reported. Impedance measurement studies between 25-65 °C under 77 % RH reveal ultrahigh proton conductivity on the order of 10^{-1}-10^{-2} S cm^{-1}. These can be regarded as important additions to the known family of high proton conducting materials. The synthesis and structural aspects of related cadmium phosphate esters, $[Cd\{OP(O)(OMe)_2\}_2\cdot(4,4'\text{-bipy})]$ and $[Cd\{OP(O)(OMe)_2\}_2\cdot(C_6H_{10}O_2N_2)]$ are summarized in chapter V; the latter being formed by *in situ* N-formylation of piperazine under solvothermal conditions in presence of DMF as solvent. The study has been extended to explore the reaction of phosphate triesters with elemental tin at elevated temperatures (180 °C). The method offers a viable route to $Me_2Sn\{OP(O)(OR')_2\}_2$, (R = Me, Et). The reactions invariably proceed *via* the concomitant formation of Sn-C and Sn-O-P bonds. A facile metal ion metathesis is observed upon the reaction of $Me_2Sn\{OP(O)(OMe)_2\}_2$ with

$Zn(OAc)_2$ under ambient conditions and resulted in the isolation of $Zn\{OP(O)(OMe)_2\}_2$ as a crystalline solid.

सार

इस थीसिस में प्रस्तुत कार्य ऑर्गेनोअमाइन मध्यस्थता वाले जिंक फॉस्फेट / फॉस्फोनेट-आधारित समन्वय संयोजनों के तर्कसंगत संश्लेषण को विकसित करने के लिए एक व्यवस्थित अध्ययन है। हाइड्रो-/सॉल्वोथर्मल प्रतिक्रियाओं में पारंपरिक ऑक्सी-फॉस्फोरस एसिड के बजाय फॉस्फेट / फॉस्फोनेट डायस्टर्स का उपयोग मध्यवर्ती चरणों के अलगाव के माध्यम से उच्च आयामी संरचनात्मक रूपांकनों की उत्पत्ति में एक अंतर्दृष्टि प्रदान करता है। कई नए कार्बनिक-अकार्बनिक संकरों को अलग किया गया है और आगे, उनके प्रोटॉन चालन व्यवहार का अध्ययन किया गया है। $[H_2Im]_2[Zn_3(HPO_3)_4]$ और $[Zn(HPO_3)(HIm)]$ जैसे संरचनात्मक ढांचे में इमिडाज़ोल/इमिडाज़ोलियम उद्धरणों को शामिल करना 10 के क्रम पर उच्च प्रोटॉन चालकता को सक्षम करने के लिए एक आंतरिक प्रोटॉन स्रोत प्रदान करता है। 10^{-3}-10^{-4} S cm^{-1} 35 पर और 77 % आरएच 25-100 °C के तापमान रेंज में। सिंथेटिक दृष्टिकोण को जिंक फॉस्फोनेट परिवार तक बढ़ा दिया गया है। परिणाम अध्याय III में वर्णित हैं। अध्याय IV में, नए कैडमियम फॉस्फाइट्स, $[Cd\{OP(O)(OH)H\}_2\cdot(4,4'\text{-bipy})]$, $[H_2pip][Cd(O_3PH)_2(H_2O)]\cdot H_2O$ और एक मिश्रित लिगैंड समन्वयन पॉलीमर, $[Cd(OAc)(ox)_{0.5}(bix)]$ ऑक्सालेट (ऑक्स) लिगैंड के स्वस्थानी गठन द्वारा निर्मित होने की सूचना है। 77% आरएच के तहत 25-65 °C के बीच प्रतिबाधा माप अध्ययन 10^{-1}-10^{-2} S cm^{-1} के क्रम पर अल्ट्राहाई प्रोटॉन चालकता को प्रकट करता है। इन्हें उच्च प्रोटॉन संवाहक सामग्री के ज्ञात परिवार के लिए महत्वपूर्ण परिवर्धन माना जा सकता है। संबंधित कैडमियम फॉस्फेट एस्टर के संश्लेषण और संरचनात्मक पहलू, $[Cd\{OP(O)(OMe)_2\}_2\cdot(4,4'\text{-bipy})]$ और $[Cd\{OP(O)(OMe)_2\}_2\cdot(C_6H_{10}O_2N_2)]$ को अध्याय V में संक्षेपित किया गया है; बाद में डीएमएफ की उपस्थिति में सॉल्वेंट के रूप में सॉल्वोथर्मल स्थितियों के तहत पाइपरज़िन के सीटू एन-फॉर्माइलेशन द्वारा गठित किया जा रहा है। अध्ययन को ऊंचा तापमान (180 °C) पर मौलिक टिन के साथ फॉस्फेट ट्राइस्टर्स की प्रतिक्रिया का पता लगाने के लिए बढ़ाया गया है। विधि $Me_2Sn\{OP(O)(OR)_2\}_2$, (R = Me, Et) के लिए एक व्यवहार्य मार्ग प्रदान करती है। प्रतिक्रियाएं हमेशा Sn-C और Sn-O-P बांड के सहवर्ती गठन के

माध्यम से आगे बढ़ती हैं। परिवेशी परिस्थितियों में $Me_2Sn\{OP(O)(OMe)_2\}_2$ के साथ $Zn(OAc)_2$ की प्रतिक्रिया पर एक सुगम धातु आयन मेटाथिसिस देखा जाता है और इसके परिणामस्वरूप $Zn\{OP(O)(OMe)_2\}_2$ का अलगाव होता है। क्रिस्टलीय ठोस के रूप में।

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GLOSSARY OF SYMBOLS AND ABBREVIATIONS

General Abbreviations

%	percent	b.p.	boiling point
°C	degree centigrade	cm	centimetre
Å	angstrom	D	dimensional
ATR	attenuated total reflectance	b.p.	boiling point
br	broad signal	h	hour
DMSO	dimethyl sulfoxide	Hz	hertz
DMF	dimethyl formamide	ICP	infinite coordination polymer
ε	molar absorptivity	λ	wavelength
e.g	for example,	μ	micro
EDX	Energy Dispersive X-ray	m.p.	melting point
ESI	electrospray ionization	RT	Room temperature
Et	ethyl	mL	milliliter
FT	Fourier transform	mmol	millimole
DMSO	dimethyl sulfoxide	e.g	for example,
DMF	dimethyl formamide	EDX	Energy Dispersive X-ray
ε	molar absorptivity	ORTEP	Oak Ridge Thermal Ellipsoid Plot
HIm	Imidazole	bix	1,4-bis((1H-imidazole-1-yl)methyl)benzene
Ph	Phenyl	mol	mole
Pip	piperazine	MOF	metal organic framework
4,4´-bipy	4,4´-bipyridine	*n*-Bu	*n*-butyl
SEM	Scanning electron microscope	nm	nanometre
TGA	thermogravimetric analysis	SDA	Structure directing agent
TMS	Tetramethyl silane	UV	ultraviolet
t-Bu	Tertiary butyl	ν	frequency
σ	conductivity	Rs	resistance
A	Area of cross-section	l	length

Molecular Structure Determination

a, b, c	Unit cell dimensions	Z	Number of molecules in the unit cell
Å	Angstrom	F(000)	Number of electrons in the unit cell

°	Degree	μ	Absorption coefficien
V	Volume of the Unit cell	ρ	Density
α, β, γ	Unit cell angles		

Spectroscopy

MS	Mass Spectroscopy	Hz	hertz
ESI	Electrospray Ionization	*J*	coupling constant
m/z	Mass per charge	m	multiplet
NMR	Nuclear magnetic resonance	d	doublet
ppm	Parts per million	t	triplet
δ	chemical shift	q	quadrat
MHz	mega hertz	IR	infrared