ORGANOTIN COORDINATION POLYMERS DERIVED FROM POLYTOPIC CARBOXYLATE LIGANDS: SYNTHESIS, GUEST INCLUSION AND SELECTIVE SENSING OF CHROMATE AND DICHROMATE IONS

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by

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Submitted

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to the

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Dedicated to My Beloved Family

CERTIFICATE

This is to certify that the thesis entitled "**ORGANOTIN COORDINATION POLYMERS DERIVED FROM POLYTOPIC CARBOXYLATE LIGANDS: SYNTHESIS, GUEST INCLUSION AND SELECTIVE SENSING OF CHROMATE AND DICHROMATE IONS**" being submitted by Ms. Archishmati Dubey 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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अति अपार जे सरित बर जौं नृप सेतु कराहिं ।
चढ़ि पिपीलिकउ परम लघु बिनु श्रम पारहि जाहिं॥

Archishmati Dubey

ABSTRACT

The work presented in this thesis is a systematic study to develop a rational synthesis of di-/trimethyltin carboxylates or tetramethyldistannoxanes by following the hydrothermal approach. The carboxylic acids used belong to the family of multifunctional ligands differing in number and relative position of -COOH groups tethered on aromatic spacers. These ligands undergo partial or complete deprotonation, depending upon the pH of the reaction medium, enabling the construction of coordination assemblies of varying compositions and topologies. The role of pH and temperature is also discernible in the organotin speciation that constitutes the assemblies.

An interesting outcome emanating from the present work is the realization of reticular synthesis based on dimeric dicarboxylatotetramethyldistannoxane, $[\{Me_2Sn(O_2C\text{-})\}_2O]_2$ as the secondary building unit (SBU). The structure of dimeric distannoxane in the two-dimensional motif, $[\{(Me_2Sn)_2O\}\{Me_2SnOSnMe_2(OH)\}btc]$ (H_3btc = 1,3,5-benzenetricarboxylic acid) is unique in respect of its composition which is derived from a symmetrical $[\{Me_2Sn(O_2C\text{-})\}_2O]$ and an unsymmetrical distannoxane $[(HO)Me_2SnOSnMe_2(O_2C\text{-})]$. The coordination frameworks are thermally and hydrolytically robust and find applications as fluorescent probes for the selective sensing of CrO_4^{2-} and $Cr_2O_7^{2-}$ ions in the aqueous medium. The study also includes the synthesis of several one-dimensional dimethyltin carboxylates using 2,2´-bipyridine and 1,10-phenanthroline as the chelating ligands. An illustrative example is $[Me_2Sn(btec)_{0.5}(2,2´\text{-bipy})]_2\cdot H_2O$ which undergoes reversible single crystal to single crystal structural transformation upon de-/rehydration of the lattice water molecules as evidenced by TGA, PXRD, and crystallographic studies. The dehydrated sample undergoes crystal structure transformation from centrosymmetric $P2_1/c$ to chiral $P2_12_12_1$ space group and reveals conformational changes in the ditin macrocycles from chair to boat form.

प्राक्कथन

इस थीसिस में प्रस्तुत कार्य हयड्रोथेरमाल संश्लेषण का पालन करके डाइ-/त्र्ये-मेथिलटिन या टेट्रामेथिलडाइस्टेंनोक्सेन के तर्कसंगत अभिक्रिया को विकसित करने के लिए एक व्यवस्थित अध्ययन है। उपयोग किये जाने वाले कार्बोक्सिलिक अम्ल बहुक्रियाशील लिगैंड्स के परिवार से सम्बंधित हैं जो एरोमेटिक स्पेसर्स पर बंधे हुए समूहों की संख्या और सापेक्ष स्तिथि में भिन्न हैं। अभिक्रिया माध्यम के पीएच के आधार पर ये लिगैंड्स आंशिक या पूर्ण अवक्षेपण से गुजरते हैं, जिससे विभिन्न रचनाओं और टोपोलॉजी के उपसहसंयोजक ढांचे के निर्माण को सक्षम किया जा सकता है। पीएच एवं तापमान की भूमिका कार्बनिकटिन प्रजाति में भी दिखाई देती है जो इन ढांचों का गठन करती हैं।

वर्तमान कार्य से निकलने वाला एक दिलचस्प परिणाम माध्यमिक निर्माण इकाई (एसबीयू) के रूप में डाइमेरिक डाइकार्बोक्सिलिकटोटेट्रामेथिलडाइस्टेंनोक्सेन, $[\{Me_2Sn(O_2C-)\}_2O]_2$ पर आधारित रैटिकुलर संश्लेषण की प्राप्ति है। द्वि-आयामी आकृति में डाइमेरिक डाइस्टैनोक्सेन की संरचना, $[\{(Me_2Sn)_2O\}\{Me_2SnOSnMe_2(OH)\}btc]$ (H_3btc = 1,3,5-बेंजीनत्र्येकार्बोक्सिलिक अम्ल) इसकी संरचना के संबंध में अद्वितीय है जो एक सममित $[\{Me_2Sn(O_2C-)\}_2O]$ और एक असममित डाइस्टैनोक्सेन $[(HO)Me_2SnOSnMe_2(O_2C-)]$ से प्राप्त होता है। उपसहसंयोजी ढांचे ऊष्मीय और हाइड्रोलाइटिक रूप से मजबूत हैं और जलीय माध्यम में CrO_4^{2-} और $Cr_2O_7^{2-}$ आयनों के चयनात्मक संवेदन के लिए फ्लोरोसेंट जांच के रूप में अनुप्रयोग किये जा सकते हैं । अध्ययन में 2,2′-बाईपिरिडीन और 1,10-फेननाथ्रोलीन को किलेटिंग लिगैंड्स के रूप में उपयोग करते हुए कई एक-आयामी डाइमेथिलटिन कार्बोक्सिलेट्स का संश्लेषण भी शामिल है। एक उदाहरण है $[Me_2Sn(btec)_{0.5}(2,2'\text{-bipy})]_2\cdot H_2O$ जो जालीय पानी के अणुओं के निर्जलीकरण/पुनर्जलीकरण पर एकल क्रिस्टल से एकल क्रिस्टल संरचनात्मक परिवर्तन से गुजरता है और TGA, PXRD एवं क्रिस्टलोग्राफिक अध्ययन द्वारा समर्थित है। निर्जलित रूपांकन सेंट्रोसिमेट्रिक $P2_1/c$ से कायरल $P2_12_12_1$ क्रिस्टल संरचना परिवर्तन से गुजरता है और डाइटिन मैक्रोसायकल के कुर्सी से नाव के रूप में परिवर्तन को प्रकट करता है।

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GLOSSARY OF SYMBOLS AND ABBREVIATIONS

General Abbreviations

BET	Brunauer-Emmett-Teller	DA	Dubinin and Astakov
MOF	Metal organic framework	D	Dimensional
SBU	Secondary building unit	FRET	Fluorescence resonance energy transfer
ORTEP	Oak Ridge Thermal Ellipsoid Plot	CP	Coordination polymer
QE	Quenching efficiency	SV	Stern-Volmer
LOD	Limit of detection	net	Network
DMSO	Dimethyl sulfoxide	THF	Tetrahydrofuran
DMF	Dimethylformamide	DCM	Dichloromethane
cy	Cyclo	Hex	Hexyl
n-Bu	Normal butyl	*t*-Bu	Tertiary butyl
Et	Ethyl	Me	Methyl
Ph	Phenyl	Bz	Benzyl
Pr	Propyl	*m*-	Meta-
o-	Ortho-	*p*-	Para-
4,4´-bipy	4,4´-Bipyridine	2,2´-bipy	2,2´-Bipyridine
phen	1,10-Phenanthroline	H_4btec	1,2,4,5-Benzenetetracarboxylic acid
H_3btc	1,3,5-Benznetricarboxylic acid	H_4ntc	1,4,5,8-Naphthalene tetracarboxylic acid
H_2pdc	Pyridinedicarboxylic acid	H_2bdc	Benzenedicarboxylic acid
H_2ntca	1,4,5,8-Naphthalenetetra carboxylic-4,5-anhydride	H_2ndc	2,6-Naphthalenedicarboxylic acid
H_2aipa	5-Aminoisphthalic acid	Σ	Sum
e.g	For example	E	Energy
%	Percent	l	Length
RT	Room temperature	h	Hour
Obsd	Observed	Calcd	Calculated

ppm	Parts per million	mL	Milliliter
cm	Centimeter	nm	Nanometer
mmol	Millimole	mm s^{-1}	Milimeter per second
mol	Mole	Hz	Hertz
°C	Degree centigrade	μ	Micro
bcu	Body-centered cubic	**sql**	Square lattice
cds	Cadmium sulfate	**hcb**	Hexagonal cubic
pcu	Primitive cubic unit		

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 coefficient
V	Volume of the Unit cell	ρ	Density
α, β, γ	Unit cell angles		

Spectroscopy

TGA	Thermogravimetric analysis	UV	Ultraviolet
SEM	Scanning electron microscope	Vis	Visible
PXRD	Powder X-ray diffraction	*J*	Coupling constant
NMR	Nuclear magnetic resonance	δ	Chemical shift
IR	Infrared	δ	Isomer shift
FT	Fourier transform	ν	Frequency
ATR	Attenuated total reflectance	λ	Wavelength
PL	Photoluminescence	ΔE_Q	Quadrupole splitting
asym	Asymmetric	sym	Symmetric