SYNTHESIS, CHARACTERIZATION AND REACTIVITY STUDIES OF ORGANOTIN ALKANESULFONATES

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DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY DELHI

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SYNTHESIS, CHARACTERIZATION AND REACTIVITY STUDIES OF ORGANOTIN ALKANESULFONATES

by

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Submitted

In fulfilment of the requirements of the degree of Doctor of Philosophy

to the

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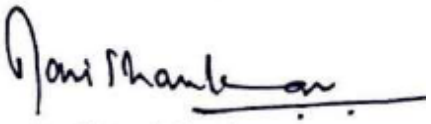
Dedicated to My Parents

CERTIFICATE

This is to certify that the thesis entitled "**SYNTHESIS, CHARACTERIZATION AND REACTIVITY STUDIES OF ORGANOTIN ALKANESULFONATES**" being submitted by Ms. Priyanka Chauhan 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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सर्वतीर्थमयी माता सर्वदेवमयः पिता
मातरं पितरं तस्मात् सर्वयत्नेन पूजयेत्

Priyanka

Priyanka Chauhan

ABSTRACT

The use of weakly coordinating oxy-sulfur anions such as triflate and arylsulfonates is quite prevalent in organotin coordination chemistry due to their varying degrees of sensitivity towards bonding with metal ions. Related chemistry derived from alkanesulfonate ligands is relatively new and provided an insight into the bonding nature of tin-sulfonate among this family and the structural attributes derived thereof. The work presented in the thesis is a systematic study to develop synthetic methods for anionic, cationic, and neutral organotin coordination frameworks associated with alkanesulfonate ligands. The stannate salts, [*n*-Bu_4N][$R_2Sn(OSO_2R^1)_3$] (R = *n*-Bu, Ph; R^1=Me, Et, *n*-Pr) are found to be promising candidates for this study being readily soluble in common organic solvents. The affinity of these ate complexes to undergo hydration/hydrolysis under ambient conditions has led to the isolation of salt cocrystals such as [$Ph_2Sn(H_2O)_4$][*n*-$Bu_4N]_2[OSO_2Me]_4$ and [*n*-$Bu_2Sn(H_2O)_4$][*n*-Bu_4N][$OSO_2Et]_3 \cdot H_2O$ which represent an unprecedented family comprising otherwise unstable tetra(aqua)diorganotin cations. The study has been extended to highlight potential antibacterial activity of these cocrystals against Gram-negative bacteria *Escherichia coli* (*E. coli*). Distinct behaviour of the stannate salts as a function of organic substituents on tin and /or sulfonate groups has been realized upon reaction with N-donor ligands. The illustrative examples include a cationic assembly, [$Ph_3Sn(L)$][OSO_2Me] (L = 1,4-bis((1H-imidazole-1- yl)methyl)benzene) following dismutation of the phenyl groups and the salt cocrystal, [*n*-$Bu_4N \cdot OSO_2Me \cdot H_2O]_2[\{(n\text{-}Bu_2Sn)_2(OH)(OSO_2Me)\}O]_2$ featuring tetraorganodistannoxane as the inorganic unit. The last chapter deals with a systematic study to address the role of solvothermal reactions in bringing about chemical transformation of *n*-$Bu_2Sn(quin)OSO_2Me$ to [(*n*-$Bu_2Sn \cdot quin)_2SO_4$] *via* cleavage of the S-C bond. The bioinorganic aspect of these mixed-ligand di-*n*-butyltin sulfates has been delineated upon interaction with calf thymus-DNA.

प्राक्कथन

धातु आयनों के साथ संबंध के प्रति संवेदनशीलता की अलग-अलग डिग्री के कारण ऑर्गोटिन समन्वय रसायन विज्ञान में कमजोर समन्वय वाले ऑक्सी-सल्फर आयनों जैसे ट्राइफलेट और आर्यलसल्फोनेट्स का उपयोग काफी प्रचलित है। अल्केनसल्फोनेट से संबंधित रसायन विज्ञान अपेक्षाकृत नया है और इस परिवार के बीच टिन-सल्फोनेट की बॉन्डिंग प्रकृति और उसके द्वारा प्राप्त संरचनात्मक विशेषताओं में एक अंतर्दृष्टि प्रदान करता है। थीसिस में प्रस्तुत काम एल्केनेसल्फोनेट लिगेंड से जुड़े आयनिक, धनिक और तटस्थ ऑर्गेनोटिन समन्वय ढांचे के लिए सिंथेटिक तरीकों को विकसित करने के लिए एक व्यवस्थित अध्ययन है। स्टैननेट लवण, [*n*-Bu_4N][$R_2Sn(OSO_2R^1)_3$] (R = *n*-Bu, Ph; R^1 = Me, Et, *n*-Pr) इस अध्ययन के लिए आशाजनक उम्मीदवार पाए जाते हैं जो आम कार्बनिक सॉल्वेंट्स में आसानी से घुलनशील होते हैं। परिवेशी परिस्थितियों में हाइड्रेशन/हाइड्रोलिसिस से गुजरने के लिए इन एट कॉम्प्लेक्स की आत्मीयता ने साल्ट कोक्रिस्टल के अलगाव को जन्म दिया है जैसे कि [Ph_2Sn (H_2O)$_4$][*n*-Bu_4N]$_2$[OSO_2Me]$_4$ और [*n*-$Bu_2Sn(H_2O)_4$][*n*-Bu_4N][OSO_2Et]$_3$·H_2O जो एक अभूतपूर्व परिवार का प्रतिनिधित्व करता है जिसमें अन्यथा अस्थिर टेट्रा (एक्वा) डायऑर्गानोटिन कैटाइअन शामिल हैं। ग्राम-नकारात्मक बैक्टीरिया *Escherichia coli (E. coli)*. के खिलाफ इन कोक्रिस्टल की संभावित जीवाणुरोधी गतिविधि को उजागर करने के लिए अध्ययन का विस्तार किया गया है। टिन और / या सल्फोनेट समूहों पर कार्बनिक पदार्थों के कार्य के रूप में स्टैनेट लवणों का विशिष्ट व्यवहार N-डोनर लिगैंड्स के साथ प्रतिक्रिया पर महसूस किया गया है। उदाहरण में Phenyl समूहों के विघटन के बाद कैटाइअनिक असेंबली [$Ph_3Sn(L)$][OSO_2Me]और अकार्बनिक यूनिट के रूप में टेट्राऑर्गनोडिस्टैनोक्सेन साल्ट कोक्रिस्टल [*n*-Bu_4N·OSO_2Me·H_2O]$_2$[{(*n*-Bu_2Sn)$_2$(OH)(OSO_2Me)}O]$_2$ शामिल हैं। अंतिम अध्याय में S-C बॉन्ड के दरार के माध्यम से *n*-Bu_2Sn(quin)OSO_2Me से [(*n*-Bu_2Sn·quin)$_2SO_4$] के रासायनिक परिवर्तन को लाने में सॉल्वोथर्मल प्रतिक्रियाओं की भूमिका को संबोधित करने के लिए एक

व्यवस्थितअध्ययन से संबंधित है। इन मिश्रित-लिगैंड [(n-Bu_2Sn·quin)$_2SO_4$] के जैव-कार्बनिक पहलू को calf thymus-DNA पर चित्रित किया गया है।

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GLOSSARY OF SYMBOLS AND ABBREVIATIONS

General Abbreviations

ORTEP	Oak Ridge Thermal Ellipsoid Plot	CP MAS	Cross Polarization Magic Angle Spinning
PDB	Protein Data Bank	OTf	Triflate
OAc	Acetate	ct-DNA	Calf thymus-DNA
THF	Tetrahydrofuran	pic	picolinate
DMSO	Dimethyl sulfoxide	quin	quinaldate
EB	Ethidium bromide	Hex	Hexyl
n-Bu	*n*-Butyl	*t*-Bu	*t*-Butyl
Et	Ethyl	Me	Methyl
Ph	Phenyl	Bu	Butyl
n-Pr	*n*-Propyl	*m*-	Meta-
o-	Ortho-	*p*-	Para-
4,4´-bipy	4,4´-Bipyridine	2,2´-bipy	2,2´-Bipyridine
pyr	Pyrazine	bix	1,4-bis((1H-imidazole-1-yl)methyl)benzene
HMPA	Hexamethylphosphoramide	*K*sv	Stern-Volmer constant
ε	Extinction coefficient	pK_a	Acidity constant
K_b	Binding constant	Hz	Hertz
b.p.	boiling point	Σ	Sum
g	gram	ns	Nanosecond
%	Percent	I	Fluorescence intensity
rt	Room temperature	h	Hour
Obsd.	Observed	Calcd.	Calculated
Eqn	Equation	V	Voltage
μ	Micro	Δ	Difference
mmol	Millimole	M	Molar concentration
°C	Degree centigrade	Bz	Benzyl

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
ESI	Electrospray Ionization	Vis	Visible
m/z	Mass per charge	*J*	Coupling constant
NMR	Nuclear magnetic resonance	δ	Chemical shift
IR	Infrared	ν	Frequency
FT	Fourier transform	λ	Wavelength
PL	Photoluminescence	s	singlet
sym	Symmetric	d	doublet
asym	Asymmetric	t	triplet
ppm	Parts per million	m	multiplet
A	Absorbance	q	quadrat