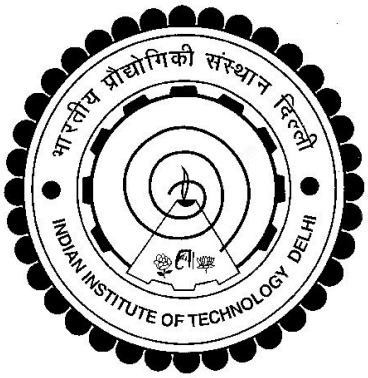
SYNTHESIS AND CHARACTERIZATION OF SUPRAMOLECULAR ASSEMBLIES BASED ON NEUTRAL AND CATIONIC METAL ALKANESULFONATES

ROHIT SINGH



DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY DELHI

OCTOBER 2017

SYNTHESIS AND CHARACTERIZATION OF SUPRAMOLECULAR ASSEMBLIES BASED ON NEUTRAL AND CATIONIC METAL ALKANESULFONATES

by

ROHIT SINGH

Submitted

In fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

to the

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY DELHI

OCTOBER 2017

Dedicated to My Family

CERTIFICATE

This is to certify that the thesis entitled "***SYNTHESIS AND CHARACTERIZATION OF SUPRAMOLECULAR ASSEMBLIES BASED ON NEUTRAL AND CATIONIC METAL ALKANESULFONATES***" being submitted by **Mr. Rohit Singh** 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 him.

Rohit Singh 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.

Dr. Ravi Shankar

Professor and Head,
Department of Chemistry,
Indian Institute of Technology,
New Delhi-110016, India.

ACKNOWLEDGEMENTS

This thesis is the result of more than 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 profound sense of gratitude to my supervisor, Prof. Ravi Shankar, for his painstaking guidance, invaluable suggestions, and above all rock-solid patience. Moreover, the full freedom to think, execute, and contribute at every stage of research, he allowed, afforded me to motivate and explore my potential, interest, and creativity in utilizing chemistry as a tool to make a difference. I am also very grateful to Guru Maa, Dr. Sukhjeevan Kaur, for providing her blessings and unconditional love sometimes in the form of sacred 'NavDurga Prasada' every year.

In addition, special thanks are due to the Head of the Chemistry Department, for providing the necessary facilities for carrying out my research work. I also extend my thanks to Prof. Jai Deo Singh for the valuable suggestions, invaluable help, and moral support on various difficult occasions.

The staff of the Instrumentation Laboratory of Chemistry Department also deserves a special mention. I would like to thank Mr. Keshav and Mr. Aalok for recording the NMR data reported in this thesis, the staff of instrumentation facility, especially Mr. Koli and Mr. Bhupender, for their help in the collection of experimental data.

In addition, thanks are also due to Prof. K. C. Molloy and Dr. G. K. Köhn (Department of Chemistry, University of Bath, UK), and Dr. Somen (IIT Delhi) for their help in single crystal X-crystallography solutions. I would also like to thank Dr. Amanpreet for her timely help and valuable suggestions.

I would also like to thank UGC, 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 colleagues (Dr. Vandana, Dr. Atul, Dr. Archana, Dr. Usha, Dr. R. P. Verma, Dr. D. K. Gupta, Ekta. Nisha, Asmita, Nidhi, Archismati, Bhawana, Swati, and Nivedita) for all those encouragements and practical advice. They have always been very supportive, friendly and eager to help. I also wish to thank my juniors (Sayantani, G. Ramu, S. Venkateshwarlu, and Mohit) for their love and genuine respect.

I convey my special thanks to Dr. Pushparaj and Dr. Sohani who always remained by my side to help and cheer me. I would also like to acknowledge my friends Dr. Kamal, Dr. Dhirendra, Dr. Manoj, and Dr. Karunesh for their good wishes and help. I have spent some of the best moments of my life with them and can never forget the love, support, and care that they provided during my stay in IIT Delhi.

Words fail to express my sentiments for my loving and respectable parents (Dr. R. S. Pal & Mrs. Sharda Pal). A Journey from rural humble background to an alumnus of IIT Kanpur and ex-stajor USSR, the benchmark set by him (personal, professional, and spiritual) always inspired me to achieve that could make him proud. Without the unconditional love, encouragement, and continuous support of my Mother, it would have been impossible for me to arrive where I am today. I deeply thank my family members (Er. Rahul, Dr. Abhilasha, Dr. Larisa) and in-laws (Mr. Ashok, Mrs. Rajni, Ashish, Manish) for the love, motivation, invaluable support that they have always shown for me. It would be difficult to conclude without mentioning my wife Parul, who deserves special thanks for bearing (all of) me with her sacrifice, care, support, and motivation during my research and difficult times. Above all, thanks to the Almighty GOD who continues to make the impossible possible.

ROHIT SINGH

ABSTRACT

The work embodied in the thesis relates to the development of new synthetic methods for the construction of metal alkanesulfonates derived from Zn(II), Mg(II), Mn(II), Cd(II), and Ag(I) ions. To this end, the known protocol involving isomerization of dialkyl sulfites, $(R'O)_2SO$ (R′ = Me, Et, ^{n}Pr) in presence of tertiary organic base or tetraalkylammonium iodide has been used for *in situ* generation of the corresponding alkanesulfonate, $(R'SO_2O)^-$ moiety. A major emphasis has been directed to synthesize coordination driven self-assemblies with direct ligand to metal bond(s) – a feature encountered rarely in the family of metal sulfonates. The role of sulfonate groups in the formation of supramolecular assemblies has been demonstrated by crystallographic studies.

The thesis is divided into five chapters. In chapter I, recent advances in the area of metal sulfonates are discussed, while chapter II relates to a detailed description of synthetic procedures and characterization methods being followed in the present study. Chapters III-V include a detailed account of the results emerging from this work.

Chapter III deals with the synthesis of new zincate salts, $[Et_3NMe]_2[Zn(OSO_2Me)_4]$ (**1**)/$[R_4N]_2[Zn(OSO_2R')_4]$ [R = Et, R′ = Me (**2**), Et (**3**); R = ^{n}Bu, R′ = ^{n}Pr (**4**)] from a one-pot reaction between anhydrous zinc(II) acetate, dialkylsulfite and tetraalkylammonium iodide. Compounds, **1-4** act as useful synthons and react with with N-donor ligands such as 4,4′-bipyridine (bipy) or 1,10-phenanthroline (phen) under inert conditions to afford the formation of neutral complexes, $[Zn(OSO_2Et)_2(bipy)(dmso)_2]$ (**5**), $[Zn(OSO_2{}^nPr)_2(bipy)_2]dmso.H_2O$ (**6**), and $[Zn(OSO_2{}^nPr)_2(phen)_2]H_2O$ (**7**). These compounds represent a scarce family of hexacoordinated zinc-based coordination frameworks with direct metal-sulfonate bonds [Zn-O(S) = 2.11-2.14 Å]. Further reactivity studies of the zincate salts with N-donor ligands in presence of trace amount of water

under ambient conditions have led to the isolation of cationic zinc complexes, $[Zn(bipy)(H_2O)_4](OSO_2Me)_2$ (**8**), $[Zn(bipy)(H_2O)_4](OSO_2Et)_2$ (**9**), $[Zn(phen)_3](OSO_2Me)_2.^nPrOH.2H_2O$ (**10**), and $[Zn(phen)_2(H_2O)_2](OSO_2Et)_2.2H_2O$ (**11**). These coordination frameworks serve as important synthons for O−H···O or C−H···O hydrogen bonding interactions and afford novel supramolecular motifs.

The studies discussed in chapter IV reveal that interesting modulations in the composition of the complexes can be achieved by reacting the zincate salts, **1-4** with water or methanol. Several coordination frameworks, $[Zn(OSO_2Me)_2(H_2O)_2]$ (**12**), $[Zn(OSO_2Me)_2(H_2O)_4]$ (**13**), $[Zn(OSO_2Et)_2(H_2O)_4]$ (**14**), $[Zn(H_2O)_6](OSO_2Et)_2$ (**15**), $[Zn(H_2O)_6](OSO_2{}^nPr)_2$ (**16**), and $[Zn(OSO_2Me)_2(MeOH)_4]$ (**17**) have been synthesized by following this approach and characterized by X-ray crystallography. The sulfonate groups in these complexes function as ambidentate ligands and act as a hub to affect hydrogen bonding interactions with coordinated water/methanol molecules. The content of this chapter also includes synthesis and structural attributes of analogous magnesium complexes, $[Mg(OSO_2Me)_2(H_2O)_2]$ (**18**), $[Mg(H_2O)_6](OSO_2Et)_2$ (**19**), and $[Mg(H_2O)_6](OSO_2{}^nPr)_2$ (**20**). These have been synthesized by reacting magnesium methoxide with dialkylsulfites in presence of tetraalkylammonium iodide. Interestingly, the cationic frameworks, $[Zn(H_2O)_6]^{2+}$ in **15**, **16** and $[Mg(H_2O)_6]^{2+}$ in **19**, **20** find ana analogy with the guanidinium-sulfonate systems in terms of execution of complementary hydrogen bonds with the alkanesulfonate counter ions.

Following the synthetic approach as described in chapter III, studies have been extended to synthesize cadmium and manganese complexes, $[Et_4N]_2[M(OSO_2Me)_4]$ [M(II) = Cd (**21**), Mn (**22**)], $[Mn(OSO_2Me)_2(H_2O)_2]$ (**23**), $[Cd(OSO_2Me)_2(H_2O)_2]$ (**24**), and $[Cd(OSO_2Me)_2(MeOH)]$ (**25**). The results are discussed in chapter V. Compound **25** represents a unique example of a layered motif resulting from μ_2 and μ_3 coordination of

the sulfonate groups. Preliminary studies have been performed to understand the role of dialkyl sulfites in the construction of coordination assemblies derived from groups 11 metal ions. The isolation of [$Ag_3(OSO_2Me)$] (**26**) represents a unique example among this family. X-ray crystal structure reveals that the asymmetric unit of **26** is composed of a trimeric cluster formed by Ag_2 and $Ag(OSO_2Me)$ fragments [Ag−Ag = 2.89 (12)−3.04 (12) Å], suggesting the presence of argentophilic and intermetallic interactions. The sulfonate group [Ag−O = 2.31 (7)–2.54 (7) Å] acts in a tetradentate fashion to extend the structure into a layered motif.

विषय-सार

थीसिस में निहित कार्य Zn(II), Mg(II), Mn(II), Cd(II), तथा Ag(I) आयन्स से बने धातु-एल्केन्स्ल्फ़ोनेट को बनाने की नवीन विधियों के विकास से संबन्धित है। अभी तक, त्रितयाक कार्बनिक बेस या टेट्राएल्काइलामोनियम आयोडाइड की मोजूदगी में डाइएलकाइल स्ल्फाइट $(R'O)_2SO$ (R' = Me, Et, ^{n}Pr) के ऐसोम्रिजेशन के ज्ञात प्रोटोकॉल का उपयोग अनुरूपनुसर एल्केन्स्ल्फ़ोनेट, $(R'SO_2O)^-$ खण्ड को यथावत उत्पन्न किया गया है। मुख्य ज़ोर लीगेण्ड से सीधे जुड़ी कोरडीनशन चालित स्वयं-संवतों के संश्लेषण पर दिया गया- एस लक्षण जो धातु सल्फोनट्स में विरल ही दिखाई पड़ता है। सुप्रमोलीकूलर एसम्ब्ली के निर्माण में सुल्फ़ोनेट ग्रुप की भूमिका को क्रिस्टीलिकर्क अध्ययन से प्रदर्शित किया गया है।

थीसिस को पाँच अध्यायो में विभाजित किया गया है। प्रथम अध्याय में धातु सल्फ़ोनेट के क्षेत्र में हुए प्रगति का वर्णन किया गया है, जबकि द्वितीय अध्याय वर्तमान अध्ययन से जुड़े संसलेशन पद्धति तथा चित्रांकण प्रणाली की विस्तृत वर्णन से संबन्धित है। तृतीय अध्याय में सुष्ख ज़िंक एसीटेट, डाइएलकाइल स्ल्फाइट, एवं टेट्राएल्काइलामोनियम आयोडाइड की एकक-पात्र अभिक्रिया द्वारा नवीन जिंककेट लवणो, $[Et_3NMe]_2[Zn(OSO_2Me)_4]$ (**1**)/$[R_4N]_2[Zn(OSO_2R')_4]$ [R = Et, R′ = Me (**2**), Et (**3**); R = ^{n}Bu, R′ = ^{n}Pr (**4**)] के सन्स्लेष्ण को वर्णित किया गया है। योगिक, **1-4** एक उपयोगी इकाई के रूप में काम करते है और N-दाता लीगण्ड जैसे की 4,4′-बाइप्रिडीन या 1,10-फिनन्थ्रोलीन के साथ निष्क्रिय दशा में अभिक्रिया कर निष्पक्ष संकुलों, $[Zn(OSO_2Et)_2(bipy)(dmso)_2]$ (**5**), $[Zn(OSO_2{}^nPr)_2(bipy)_2]dmso.H_2O$ (**6**), and $[Zn(OSO_2{}^nPr)_2(phen)_2]H_2O$ (**7**) के निर्माण को प्राप्त किया गया है। ये योगिक दुर्लभ प्रत्यक्ष धातु-लीगण्ड बन्ध वाले [Zn-O(S) = 2.11-2.14 Å] सश्ठ्सन्योजित ज़िंक आधारित संयोजित संरचना को प्रदर्शित करते हैं। इसके अतिरिक्त अभिक्रिया अध्ययन में जिंककेट लवणो की N-दाता लीगण्ड के साथ अवशेषी नमी परिवेशी दशा में ध्न्यात्मक ज़िंक संकुलो $[Zn(bipy)(H_2O)_4](OSO_2Me)_2$ (**8**), $[Zn(bipy)(H_2O)_4](OSO_2Et)_2$ (**9**), $[Zn(phen)_3](OSO_2Me)_2.{}^nPrOH.2H_2O$ (**10**), and $[Zn(phen)_2(H_2O)_2](OSO_2Et)_2.2H_2O$ (**11**) का बनना दिखाया गया है। ये संयोजित संरचना O−H···O या C−H···O हाइड्रोजन बन्ध की महत्वपूर्ण इकाई का कार्य तथा नवीन सुप्रमोलीकूलर अनुकल्प के बनती है। चतुर्थ अध्याय में वर्णित अध्ययनों से प्रदर्शित होता है की जिंककेट लवणो **1-4** की जल या मिथेनोल से अभिक्रिया कर योगिकों के संघटन में रोचक परिवर्तन को प्राप्त किया जा सकता है। इस प्द्यती का अनुकरण कर कई संयोजित संरचना, $[Zn(OSO_2Me)_2(H_2O)_2]$ (**12**), $[Zn(OSO_2Me)_2(H_2O)_4]$ (**13**),

$[Zn(OSO_2Et)_2(H_2O)_4]$ (**14**), $[Zn(H_2O)_6](OSO_2Et)_2$ (**15**), $[Zn(H_2O)_6](OSO_2{}^nPr)_2$ (**16**), and $[Zn(OSO_2Me)_2(MeOH)_4]$ (**17**) का संश्लेषण किया गया तथा एक्स-रे क्रिस्टलोग्रफी द्वारा विश्लेषित किया गया है। सल्फ़ोनेट ग्रुप इन संकुलों म अंबिडेंटेट लीगण्ड की तरह कार्य करता है तथा संकुलित जल/मिथेनोल अणुओ के साथ हाइड्रोजन बन्ध बनाने के केंद्र के रूप में काम करता है। इस अध्याय के विषय-वस्तु में मेग्नीशियम संकुलों, $[Mg(OSO_2Me)_2(H_2O)_2]$ (**18**), $[Mg(H_2O)(OSO_2Et)_2$ (**19**), and $[Mg(H_2O)_6](OSO_2{}^nPr)_2$ (**20**) के अनुरूपों की संश्लेशात्मक तथा संरचनात्मक विशेषताओं को भी समाहित किया गया है। **इनको** मेग्नीशियम मिथोक्साइड की डाइएलकाइल स्ल्फाइट के साथ टेट्राएल्काइलामोनियम आयोडाइड की मोजूदगी में अभिक्रिया कर संसलेशित किया गया। रोचक रूप में **15**, **16** की $[Zn(H_2O)_6]^{2+}$ तथा **19**, **20** की $[Mg(H_2O)_6]^{2+}$ की धनात्मक संरचना इकाई एल्केन्स्ल्फ़ोनेट काउंटर आयनों के साथ संपूरक हाइड्रोजन बन्धो के निष्पादन करने के संबंध में गुयानिडीनियम-सुल्फ़ोनेट तंत्र की अनुरूपता को दिखाता है। पंचम अध्याय में पूर्व संसलेशन विधि का उपयोग कर केडमियम तथा मेंगनीज़ संकुलों $[Et_4N]_2[M(OSO_2Me)_4]$ [M(II) = Cd (**21**), Mn (**22**)], $[Mn(OSO_2Me)_2(H_2O)_2]$ (**23**), $[Cd(OSO_2Me)_2(H_2O)_2]$ (**24**), and $[Cd(OSO_2Me)_2(MeOH)]$ (**25**).को बनाया गया है। योगिक **25 में** सुल्फ़ोनेट ग्रुप की μ_2 तथा μ_3 की संयोजकता के फलस्वरूप परतीय इकाई का अनुपम प्रदर्शित हुआ है। $[Ag_3(OSO_2Me)]$ (**26**) का संश्लेषण उपरोक्त संकुलों के परिवार में ग्रुप 11 का अनुपम उदाहरण है। योगिक 26 के एक्स-रे क्रिस्टल संरचना त्रिपरमाणु आकृति को दिखाता है जो की Ag_2 **तथा** $Ag(OSO_2Me)$ खंडो से जुड़ कर बनी हुई दिखाई पड़ती हैं। बन्ध दूरी [$Ag{-}Ag$ = 2.89 (12)−3.04 (12) Å] अर्जेंटोफिलिक तथा इंटेर्मेटललिक प्रभावों को प्रदर्शित करता है। सुल्फ़ोनेट ग्रुप की टेट्राडेंटेट आचरण [$Ag{-}O$ = 2.31 (7)–2.54 (7) Å]से संरचना को परतीय रूप मिलता है।

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

Chapter IV

Chapter V

Glossary of Symbols and Abbreviations

Å	angstroms
%	percent
°	degree
μ	micro
δ	chemical shift
°C	degree centigrade
ATR	attenuated total reflectance
b.p.	boiling point
bipy	4,4′-bipyridine
br	broad signal
$CDCl_3$	deuterated chloroform
cm	centimeter
CP	coordination polymer
D	dimensional
d	doublet
dmso-d_6	deuterated dimethylsulfoxide
eqn.	equation
ESI	electrospray-ionization
Et	ethyl
Et_2O	diethyl ether
Et_3N	triethylamine
FT-IR	Fourier transform infra-red
g	gram
h	hour
Hz	Hertz

i.e	that is
J	coupling constant
m	multiplet
m/z	mass/charge
Me	methyl
MeOH	methanol
MHz	mega Hertz
mL	milliliter
mmol	millimole
MOF	metal-organic framework
mol	mole
^{n}Bu	*n*-butyl
NMR	nuclear magnetic resonance
^{n}Pr	*n*-propyl
^{n}PrOH	*n*-propanol
OAc	acetate
ORTEP	Oak Ridge Thermal Ellipsoid Plot
phen	1,10-phenanthroline
q	quartet
rt	room temperature
s	singlet
SC-XRD	single crystal x-ray diffraction
t	triplet
λ	wavelength
v	frequency