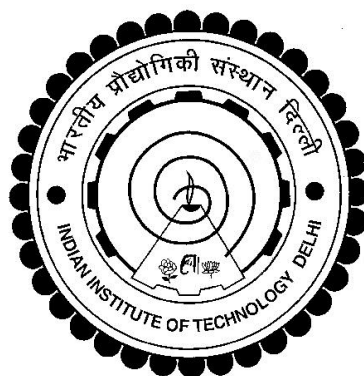


**SYNTHESIS AND CHARACTERIZATION OF
SUPRAMOLECULAR ASSEMBLIES BASED ON NEUTRAL
AND CATIONIC METAL ALKANESULFONATES**

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**

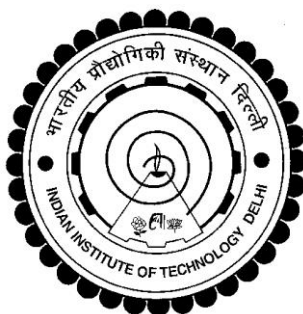
by

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. Dharendra, 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, $(R'O)_2SO$ ($R' = \text{Me, Et, } ^n\text{Pr}$) 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, $[\text{Et}_3\text{NMe}]_2[\text{Zn}(\text{OSO}_2\text{Me})_4]$ (**1**)/ $[\text{R}_4\text{N}]_2[\text{Zn}(\text{OSO}_2\text{R}')_4]$ [$\text{R} = \text{Et}$, $\text{R}' = \text{Me}$ (**2**), Et (**3**); $\text{R} = ^n\text{Bu}$, $\text{R}' = ^n\text{Pr}$ (**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 N-donor ligands such as 4,4'-bipyridine (bipy) or 1,10-phenanthroline (phen) under inert conditions to afford the formation of neutral complexes, $[\text{Zn}(\text{OSO}_2\text{Et})_2(\text{bipy})(\text{dmsO})_2]$ (**5**), $[\text{Zn}(\text{OSO}_2^n\text{Pr})_2(\text{bipy})_2]\text{dmsO} \cdot \text{H}_2\text{O}$ (**6**), and $[\text{Zn}(\text{OSO}_2^n\text{Pr})_2(\text{phen})_2]\text{H}_2\text{O}$ (**7**). These compounds represent a scarce family of hexacoordinated zinc-based coordination frameworks with direct metal-sulfonate bonds $[\text{Zn}-\text{O}(\text{S}) = 2.11\text{-}2.14 \text{ \AA}]$. 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, $[\text{Zn}(\text{bipy})(\text{H}_2\text{O})_4](\text{OSO}_2\text{Me})_2$ (**8**), $[\text{Zn}(\text{bipy})(\text{H}_2\text{O})_4](\text{OSO}_2\text{Et})_2$ (**9**), $[\text{Zn}(\text{phen})_3](\text{OSO}_2\text{Me})_2 \cdot n\text{PrOH} \cdot 2\text{H}_2\text{O}$ (**10**), and $[\text{Zn}(\text{phen})_2(\text{H}_2\text{O})_2](\text{OSO}_2\text{Et})_2 \cdot 2\text{H}_2\text{O}$ (**11**). These coordination frameworks serve as important synthons for O–H $\cdots$ O or C–H $\cdots$ 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, $[\text{Zn}(\text{OSO}_2\text{Me})_2(\text{H}_2\text{O})_2]$ (**12**), $[\text{Zn}(\text{OSO}_2\text{Me})_2(\text{H}_2\text{O})_4]$ (**13**), $[\text{Zn}(\text{OSO}_2\text{Et})_2(\text{H}_2\text{O})_4]$ (**14**), $[\text{Zn}(\text{H}_2\text{O})_6](\text{OSO}_2\text{Et})_2$ (**15**), $[\text{Zn}(\text{H}_2\text{O})_6](\text{OSO}_2^i\text{Pr})_2$ (**16**), and $[\text{Zn}(\text{OSO}_2\text{Me})_2(\text{MeOH})_4]$ (**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, $[\text{Mg}(\text{OSO}_2\text{Me})_2(\text{H}_2\text{O})_2]$ (**18**), $[\text{Mg}(\text{H}_2\text{O})_6](\text{OSO}_2\text{Et})_2$ (**19**), and $[\text{Mg}(\text{H}_2\text{O})_6](\text{OSO}_2^i\text{Pr})_2$ (**20**). These have been synthesized by reacting magnesium methoxide with dialkylsulfites in presence of tetraalkylammonium iodide. Interestingly, the cationic frameworks, $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ in **15**, **16** and $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ in **19**, **20** find an 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, $[\text{Et}_4\text{N}]_2[\text{M}(\text{OSO}_2\text{Me})_4]$ [$\text{M}(\text{II}) = \text{Cd}$ (**21**), Mn (**22**)], $[\text{Mn}(\text{OSO}_2\text{Me})_2(\text{H}_2\text{O})_2]$ (**23**), $[\text{Cd}(\text{OSO}_2\text{Me})_2(\text{H}_2\text{O})_2]$ (**24**), and $[\text{Cd}(\text{OSO}_2\text{Me})_2(\text{MeOH})]$ (**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 $[\text{Ag}_3(\text{OSO}_2\text{Me})]$ (**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 $\text{Ag}(\text{OSO}_2\text{Me})$ fragments [$\text{Ag}-\text{Ag} = 2.89(12)-3.04(12) \text{ \AA}$], suggesting the presence of argentophilic and intermetallic interactions. The sulfonate group [$\text{Ag}-\text{O} = 2.31(7)-2.54(7) \text{ \AA}$] 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-एल्केन्सुल्फोनेट को बनाने की नवीन विधियों के विकास से संबन्धित है। अभी तक, त्रितयाक कार्बनिक बेस या टेट्राएल्काइलामोनियम आयोडाइड की मौजूदगी में डाइएलकाइल स्ल्फाइड (R'O)₂SO (R' = Me, Et, ⁿPr) के एसोमिजेशन के ज्ञात प्रोटोकॉल का उपयोग अनुरूपनुसर एल्केन्सुल्फोनेट, (R'SO₂O)⁻ खण्ड को यथावत उत्पन्न किया गया है। मुख्य जोर लीगेण्ड से सीधे जुड़ी कोरडीनशन चालित स्वयं-संवर्तों के संश्लेषण पर दिया गया- एस लक्षण जो धातु सल्फोनट्स में विरल ही दिखाई पड़ता है। सुप्रमोलीकूलर एसम्ब्ली के निर्माण में सुल्फोनेट ग्रुप की भूमिका को क्रिस्टीलिकर्क अध्ययन से प्रदर्शित किया गया है।

थीसिस को पाँच अध्यायों में विभाजित किया गया है। प्रथम अध्याय में धातु सल्फोनेट 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 सुष्व जिंक एसीटेट, डाइएलकाइल स्ल्फाइड, एवं टेट्राएल्काइलामोनियम आयोडाइड की एकक-पात्र अभिक्रिया द्वारा नवीन जिंककेट लवणों, [Et₃NMe]₂[Zn(OSO₂Me)₄] (1)/[R₄N]₂[Zn(OSO₂R')₄] [R = Et, R' = Me (2), Et (3); R = ⁿBu, R' = ⁿPr (4)] के संसलेशन को वर्णित किया गया है। योगिक, 1-4 एक उपयोगी इकाई के रूप में काम करते हैं और N-दाता लीगेण्ड जैसे की 4,4'-बाइप्रिडीन या 1,10-फिनन्थ्रोलीन के साथ निष्क्रिय दशा में अभिक्रिया कर निष्पक्ष संकुलों, [Zn(OSO₂Et)₂(bipy)(dmsO)₂] (5), [Zn(OSO₂ⁿPr)₂(bipy)₂]dmsO.H₂O (6), and [Zn(OSO₂ⁿPr)₂(phen)₂]H₂O (7) के निर्माण को प्राप्त किया गया है। ये योगिक दुर्लभ प्रत्यक्ष धातु-लीगेण्ड बन्ध वाले [Zn-O(S) = 2.11-2.14 Å] सश्रुसन्योजित जिंक आधारित संयोजित संरचना को प्रदर्शित करते हैं। इसके अतिरिक्त अभिक्रिया अध्ययन में जिंककेट लवणों की N-दाता लीगेण्ड के साथ अवशेषी नमी परिवेशी दशा में धन्यात्मक जिंक संकुलों [Zn(bipy)(H₂O)₄](OSO₂Me)₂ (8), [Zn(bipy)(H₂O)₄](OSO₂Et)₂ (9), [Zn(phen)₃](OSO₂Me)₂.ⁿPrOH.2H₂O (10), and [Zn(phen)₂(H₂O)₂](OSO₂Et)₂.2H₂O (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 लवणों 1-4 की जल या मिथेनोल से अभिक्रिया कर योगिकों के संघटन में रोचक परिवर्तन को प्राप्त किया जा सकता है। इस पद्धति का अनुकरण कर कई संयोजित संरचना, [Zn(OSO₂Me)₂(H₂O)₂] (12), [Zn(OSO₂Me)₂(H₂O)₄] (13),

$[\text{Zn}(\text{OSO}_2\text{Et})_2(\text{H}_2\text{O})_4]$ (14), $[\text{Zn}(\text{H}_2\text{O})_6](\text{OSO}_2\text{Et})_2$ (15),
 $[\text{Zn}(\text{H}_2\text{O})_6](\text{OSO}_2^i\text{Pr})_2$ (16), and $[\text{Zn}(\text{OSO}_2\text{Me})_2(\text{MeOH})_4]$ (17) का संश्लेषण किया
 गया तथा एक्स-रे क्रिस्टलोग्राफी द्वारा विश्लेषित किया गया है। सुल्फोनेट ग्रुप इन संकुलों में अंबिडेंट लीगण्ड की तरह कार्य
 करता है तथा संकुलित जल/मिथेनॉल अणुओं के साथ हाइड्रोजन बन्ध बनाने के केंद्र के रूप में काम करता है। इस अध्याय
 के विषय-वस्तु में मैग्नीशियम संकुलों, $[\text{Mg}(\text{OSO}_2\text{Me})_2(\text{H}_2\text{O})_2]$ (18), $[\text{Mg}(\text{H}_2\text{O})_6](\text{OSO}_2\text{Et})_2$
 (19), and $[\text{Mg}(\text{H}_2\text{O})_6](\text{OSO}_2^i\text{Pr})_2$ (20) के अनुरूपों की संश्लेषात्मक तथा संरचनात्मक विशेषताओं
 को भी समाहित किया गया है। इनको मैग्नीशियम मिथोक्साइड की डाइएलकाइल स्ल्फाइड के साथ टेट्राएल्कामोनियम
 आयोडाइड की मौजूदगी में अभिक्रिया कर संसलेशित किया गया। रोचक रूप में 15, 16 की $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ तथा
 19, 20 की $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ की धनात्मक संरचना इकाई एल्केन्सुल्फोनेट काउंटर आयनों के साथ संपूरक हाइड्रोजन
 बन्धों के निष्पादन करने के संबंध में गुयानिडीनियम-सुल्फोनेट तंत्र की अनुरूपता को दिखाता है। पंचम अध्याय में पूर्व
 संसलेशन विधि का उपयोग कर केडमियम तथा मैंगनीज संकुलों $[\text{Et}_4\text{N}]_2[\text{M}(\text{OSO}_2\text{Me})_4]$ $[\text{M(II)} = \text{Cd}$
 (21), Mn (22)], $[\text{Mn}(\text{OSO}_2\text{Me})_2(\text{H}_2\text{O})_2]$ (23), $[\text{Cd}(\text{OSO}_2\text{Me})_2(\text{H}_2\text{O})_2]$ (24),
 and $[\text{Cd}(\text{OSO}_2\text{Me})_2(\text{MeOH})]$ (25) को बनाया गया है। योगिक 25 में सुल्फोनेट ग्रुप की μ_2 तथा μ_3
 की संयोजकता के फलस्वरूप परतीय इकाई का अनुपम प्रदर्शित हुआ है। $[\text{Ag}_3(\text{OSO}_2\text{Me})]$ (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 $\text{Ag}(\text{OSO}_2\text{Me})$ खंडों से जुड़ कर बनी हुई दिखाई पड़ती है। बन्ध दूरी $[\text{Ag}-\text{Ag} =$
 2.89 (12)– 3.04 (12) Å] अर्जेंटोफिलिक तथा इंटेर्मेटलिक प्रभावों को प्रदर्शित करता है। सुल्फोनेट ग्रुप की
 टेट्राडेंट आचरण $[\text{Ag}-\text{O} = 2.31$ (7)– 2.54 (7) Å] से संरचना को परतीय रूप मिलता है।

TABLE OF CONTENTS

	Page No.
<i>Certificate</i>	<i>i</i>
<i>Acknowledgements</i>	<i>ii</i>
<i>Abstract</i>	<i>iv</i>
<i>Table of Contents</i>	<i>vii</i>
<i>List of Figures</i>	<i>viii</i>
<i>List of Tables</i>	<i>xii</i>
<i>Glossary of Symbols and Abbreviations</i>	<i>xv</i>
 CHAPTER I Introduction	 1-11
Scope and aim	12
 CHAPTER II Materials and Methods	 14-26
 CHAPTER III Synthesis and characterization of zinc alkanesulfonates bearing N-donor ligands	 27-62
 CHAPTER IV Synthesis and characterization of Zn(II) and Mg(II) alkanesulfonates	 63-97
 CHAPTER V Synthesis and characterization of metal methanesulfonates based on Mn(II), Cd(II), and Ag(I) ions	 98-115
 SUMMARY	 116-118
 REFERENCES	 119-129
 APPENDIX Figures	 130-140
 BIO-DATA OF THE AUTHOR	

LIST OF FIGURES

Figure No.	Description	Page No.
Chapter III		
3.1	Hydrogen bond interactions between the symmetrical sulfonate anions and guanidinium cations	28
3.2	^1H (top) and $^{13}\text{C}\{^1\text{H}\}$ (bottom) NMR spectra of 4	33
3.3	(a) ORTEP drawing of 5 with 50% probability level (b) A perspective 3D view showing H-bond interactions (blue dash lines) in <i>bc</i> -plane. The ethyl groups and hydrogen atoms of pyridyl rings are omitted for clarity	38
3.4	(a) ORTEP drawing of 6 with 50% probability level (b) A perspective 3D view showing H-bond interactions (blue dash lines) in <i>bc</i> -plane. The <i>n</i> -propyl groups and hydrogen atoms of pyridyl rings are omitted for clarity	40
3.5	(a) ORTEP drawing of the structure of 7 with 50% probability level. (b) Perspective view of the hydrogen bonds in <i>ab</i> -plane (blue dash lines) (c) A perspective 3D view in <i>ac</i> -plane. <i>n</i> -Propyl groups and hydrogen atoms of aromatic rings are omitted for clarity	41
3.6	(a) ORTEP drawing of 8 with 50% probability level. Hydrogen atoms of pyridyl rings are omitted for clarity. (b) Perspective view of the hydrogen bonds (blue dash lines). (c) A perspective 3D view in <i>ab</i> -plane	46
3.7	(a) ORTEP drawing of 9 with 50% probability level. Hydrogen atoms of ethyl and pyridyl rings are omitted for clarity. (b) A 3D view of 9 in <i>ab</i> -plane with hydrogen bonds (blue dash lines).	47
3.8	(a) ORTEP drawing of 10 with 50% probability level (b) Hydrogen atoms are omitted for clarity. (b), (c), and (d) Perspective views of the hydrogen bond, π - π , and anion- π	49

Figure No.	Description	Page No.
	interactions respectively (e) 3D view of 10 in <i>bc</i> -plane.	
3.9	(a) ORTEP drawing of 11 with 50% probability level. Hydrogen atoms of aromatic rings are omitted for clarity. (b) and (c) Perspective views of hydrogen bond and π – π interactions, respectively. (d) The 3D structure of 10 in <i>bc</i> -plane	51
A1	IR (cm ⁻¹) spectrum of [Et ₄ N] ₂ [Zn(OSO ₂ Et) ₄] (3)	127
A2	Thermogravimetric graph of [Zn(OSO ₂ Et) ₂ (bipy)(dmsO) ₂] (5)	128
A3	Thermogravimetric graph of [Zn(H ₂ O) ₄ (bipy)](OSO ₂ Et) ₂ (9)	129
A4	IR (cm ⁻¹) spectrum of [Zn(H ₂ O) ₄ (bipy)](OSO ₂ Et) ₂ (9)	130

Chapter IV

4.1	ORTEP drawing of the perspective 2D view of 12 showing hydrogen bonds (blue dash lines) in <i>ab</i> -plane with 50% probability level. Methyl groups are omitted for clarity	67
4.2	(a) ORTEP drawing of 13 with 50% probability level. (b) Perspective 2D view showing hydrogen bonds (blue dash lines) in <i>bc</i> -plane. Methyl groups are omitted for clarity.	69
4.3	(a) ORTEP drawing of 14 with 50% probability level. Hydrogen atoms of ethyl groups are omitted for clarity. (b) Perspective 2D view showing hydrogen bonds (blue dash lines) in <i>ab</i> -plane. Ethyl groups are omitted for clarity	70
4.4	(a) ORTEP drawing of 15 with 50% probability level. (b) Perspective view of hydrogen bonds (blue dash lines) interactions. Ethyl groups are omitted for clarity. (c) Perspective 3D view in <i>bc</i> -plane	72
4.5	(a) ORTEP drawing of 16 with 50% probability level. (b) A perspective view showing hydrogen bond interactions (blue dash lines). Propyl groups are omitted for clarity. (c)	73

Figure No.	Description	Page No.
	Perspective 3D view in <i>ab</i> -plane	
4.6	(a) ORTEP drawing of 17 with 50% probability level. Hydrogen atoms of methyl groups are omitted for clarity. (b) Perspective 2D view showing hydrogen bond interactions (blue dash lines) in <i>bc</i> -plane. Methyl groups are omitted for clarity	75
4.7	(a) ORTEP drawing of 18 with 50% probability level. (b) A perspective view of 2D layer showing hydrogen bond interactions (blue dash lines) in <i>ab</i> -plane	80
4.8	(a) ORTEP drawing of 19 with 50% probability level. (b) Perspective view of hydrogen bond interactions (blue dash lines) in <i>bc</i> -plane. Ethyl groups are omitted for clarity. (c) Perspective 3D view in <i>ac</i> -plane	82
4.9	(a) ORTEP drawing of 20 with 50% probability level. (b) Perspective view of hydrogen bond interactions (blue dash lines). Propyl groups are omitted for clarity. (c) Perspective 3D view of in <i>ab</i> -plane	84
A5	Thermogravimetric graph of $[\text{Zn}(\text{H}_2\text{O})_6](\text{OSO}_2\text{Et})_2$ (15)	131
A6	IR (cm^{-1}) spectrum of $[\text{Zn}(\text{H}_2\text{O})_6](\text{OSO}_2\text{Et})_2$ 15	132
A7	^1H (top)and $^{13}\text{C}\{^1\text{H}\}$ (bottom) NMR spectra of $[\text{Zn}(\text{H}_2\text{O})_6](\text{OSO}_2^i\text{Pr})_2$ (16). (Residual signals of <i>dms</i> <i>o</i> - <i>d</i> ₆ are marked with X)	133
A8	IR (cm^{-1}) spectrum of $[\text{Zn}(\text{OSO}_2\text{Me})_2(\text{MeOH})_4]$ (17)	134
A9	Thermogravimetric graph of $[\text{Mg}(\text{OSO}_2\text{Me})_2(\text{H}_2\text{O})_2]$ (18)	135

Chapter V

5.1	ORTEP drawing of the 2D view of 23 showing hydrogen bonds (blue dash lines) in <i>ab</i> -plane with 50% probability level. Methyl groups are omitted for clarity	103
5.2	ORTEP drawing of the 2D view of 24 showing hydrogen	104

Figure No.	Description	Page No.
	bonds (blue dash lines) in <i>ab</i> -plane. Methyl groups are omitted for clarity	
5.3	(a) ORTEP drawing of the asymmetric unit of 25 with 50% probability level. (b) Perspective 2D view of the coordinative environment around each cadmium atom (green spheres) and the bonding modes (μ_2 and μ_3) of sulfonate ligands (yellow spheres) in <i>ab</i> -plane. Perspective 3D view of showing hydrogen bonds (blue dash lines) in <i>ac</i> -plane.	105
5.4	(a) ORTEP drawing of the asymmetric unit of 26 with 50% probability level. (b) Perspective view of the 2D layer formed by interactions between silver atoms. Sulfonate groups are omitted for clarity (c) Perspective 3D view showing hydrogen bond interactions (blue dash lines).	108
A10	^1H NMR spectrum of $[\text{Cd}(\text{OSO}_2\text{Me})_2(\text{MeOH})]$ (25) (Residual signals of dms- d_6 are marked with stars)	136
A11	Thermogravimetric analysis graph of $[\text{Cd}(\text{OSO}_2\text{Me})_2(\text{MeOH})]$ (25)	137

LIST OF TABLES

Table No.	Chapter III	Page No.
	Description	
3.1	ESI-MS (negative ion mode) spectral data of 1–4	31
3.2	IR (cm ⁻¹), ¹ H and ¹³ C{ ¹ H} NMR spectral data (δ, ppm) of 1–4	32
3.3	IR (cm ⁻¹), ¹ H NMR and ¹³ C{ ¹ H} spectral data (δ, ppm) of 5-7	36
3.4	IR (cm ⁻¹), ¹ H and ¹³ C{ ¹ H} NMR spectral data (δ, ppm) of 8-11	45
3.5	Summary of the crystallographic data for 5-7	53
3.6	Selected bond lengths (Å) and bond angles (°) for 5	54
3.7	Hydrogen bond parameters of 5	54
3.8	Selected bond lengths (Å) and bond angles (°) for 6	55
3.9	Hydrogen bond parameters of 6	55
3.10	Selected bond lengths (Å) and bond angles (°) for 7	56
3.11	Hydrogen bond parameters of 7	56
3.12	Summary of the crystallographic data for 8 and 9	57
3.13	Summary of the crystallographic data for 10 and 11	58
3.14	Selected bond lengths (Å) and bond angles (°) for 8	59
3.15	Hydrogen bond parameters of 8	59
3.16	Selected bond lengths (Å) and bond angles (°) for 9	60
3.17	Hydrogen bond parameters of 9	60
3.18	Selected bond lengths (Å) and bond angles (°) for 10	61
3.19	Hydrogen bond parameters of 10	61
3.20	Selected bond lengths (Å) and bond angles (°) for 11	62
3.21	Hydrogen bond parameters of 11	62

Chapter IV

4.1	IR (cm ⁻¹), ¹ H NMR and ¹³ C{ ¹ H} spectral data (δ, ppm) of 12-17	66
4.2	IR (cm ⁻¹), ¹ H NMR and ¹³ C{ ¹ H} spectral data (δ, ppm) of 18-20	79
4.3	Summary of the crystallographic data for 12-14	86
4.4	Summary of the crystallographic data for 15-17	87
4.5	Summary of the crystallographic data for 18-20	88
4.6	Selected bond lengths (Å) and bond angles (°) for 12	89
4.7	Hydrogen bond parameters of 12	89
4.8	Selected bond lengths (Å) and bond angles (°) for 13	90
4.9	Hydrogen bond parameters of 13	90
4.10	Selected bond lengths (Å) and bond angles (°) for 14	91
4.11	Hydrogen bond parameters of 14	91
4.12	Selected bond lengths (Å) and bond angles (°) for 15	92
4.13	Hydrogen bond parameters of 15	92
4.14	Selected bond lengths (Å) and bond angles (°) for 16	93
4.15	Hydrogen bond parameters of 16	93
4.16	Selected bond lengths (Å) and bond angles (°) for 17	94
4.17	Hydrogen bond parameters of 17	94
4.18	Selected bond lengths (Å) and bond angles (°) for 18	95
4.19	Hydrogen bond parameters of 18	95
4.20	Selected bond lengths (Å) and bond angles (°) for 19	96
4.21	Hydrogen bond parameters of 19	96
4.22	Selected bond lengths (Å) and bond angles (°) for 20	97
4.23	Hydrogen bond parameters of 20	97

Chapter V

5.1	ESI-MS (negative ion mode) spectral data of 21 and 22	100
5.2	Summary of crystallographic data of 23-25	110
5.3	Selected bond lengths (Å) and bond angles (°) for 23	111

5.4	Hydrogen bond parameters of 23	111
5.5	Selected bond lengths (Å) and bond angles (°) for 24	112
5.6	Hydrogen bond parameters of 24	112
5.7	Selected bond lengths (Å) and bond angles (°) for 25	113
5.8	Hydrogen bond parameters of 25	113
5.9	Summary of crystallographic data of 26	114
5.10	Selected bond lengths (Å) and bond angles (°) for 26	115
5.11	Hydrogen bond parameters of 26	115

SUMMARY

S-1	Comprehensive list of compounds and their structural details.	117
-----	---	-----

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
dms -- <i>d</i> ₆	deuterated dimethylsulfoxide
eqn.	equation
ESI	electrospray-ionization
Et	ethyl
Et ₂ O	diethyl ether
Et ₃ N	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	<i>n</i> -butyl
NMR	nuclear magnetic resonance
ⁿ Pr	<i>n</i> -propyl
ⁿ PrOH	<i>n</i> -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
ν	frequency
