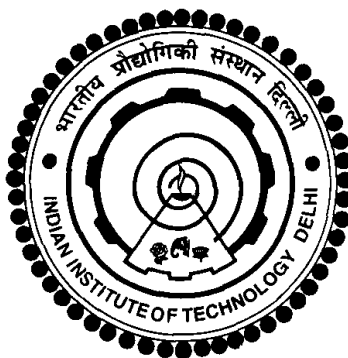


**DESIGN AND SYNTHESIS OF N- AND S/Se SUBSTITUTED  
ORGANIC SPECIES AND THEIR EXCEPTIONAL BEHAVIOR  
TOWARDS  $d^{10}$  METAL IONS,  $UO_2^{2+}$  ION AND ORGANIC  
GUEST MOLECULES**

**JAGRITI SINGH**



**DEPARTMENT OF CHEMISTRY  
INDIAN INSTITUTE OF TECHNOLOGY DELHI  
AUGUST 2019**



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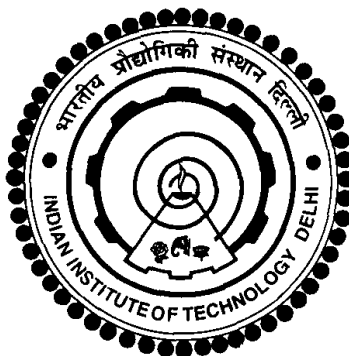
**JAGRITI SINGH**

**DEPARTMENT OF CHEMISTRY**

**Submitted**

**In fulfillment of the requirements of the degree of Doctor of Philosophy**

**to the**



**INDIAN INSTITUTE OF TECHNOLOGY DELHI**

**AUGUST 2019**



***Dedicated to***

***All that I am, or hope to be, I owe to my angelic***

***Mami Mrs. Chhaya Singh and***

***Mama Dr. Raghvendra Pratap Singh***

***and***

***In memory of my beloved parents***

***Arun Kumar Singh and Sudha Singh***

***(Heavenly abode)***



## ***Certificate***

*This is to certify that the thesis entitled, “Design and Synthesis of N- and S/Se- Substituted Organic Species and Their Exceptional Behavior Towards  $d^{10}$  Metal Ions,  $UO_2^{2+}$  Ion and Organic Guest Molecules” being submitted by Ms. Jagriti Singh, to the Indian Institute of Technology Delhi for the award of degree of ‘Doctor of Philosophy’ in Chemistry is a bonafide research work carried out by her. Ms. Jagriti Singh has worked under my guidance and supervision and has fulfilled the requirements for the submission of 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 award of any degree or diploma.*

*Date:*

***Dr. Jai Deo Singh***  
*Professor*  
*Department Chemistry*  
*Indian Institute of Technology Delhi*  
*New Delhi- 110016*



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*Jagrithi Singh*

## ABSTRACT

The thesis entitled “*Design and Synthesis of N- and S/Se- Substituted Organic Species and Their Exceptional Behavior Towards  $d^{10}$  Metal Ions,  $UO_2^{2+}$  Ion and Organic Guest Molecules*” describes the synthesis of new kind of organic heteroatom donor species or architectures modified by incorporating chalcogen atoms, mainly sulfur, with controlled geometries and new arrangement of donor atoms to understand their behavior towards  $d^{10}$  metal ions,  $UO_2^{2+}$  ion and organic guest molecules.

**Chapter I** provides a brief overview as introductory remarks on ligand design aspects from acyclic to cyclic analogue bearing heteroatom donor combinations and their potential applications in various fields that have been realized in past two and half decades. It also explains aims and objectives of present research work.

**Chapter II** provides the list of chemicals and reagent used throughout the research work and details of the synthetic methodology adopted for the preparation of starting materials that are not commercially available. It also explains various physicochemical and spectroscopic studies used for the characterization of newly synthesized compounds.

**Chapter III** deals with the synthesis of 1,2,3-triazole based acyclic organic donors bearing heteroatomic N, S/Se donor combinations in their structural framework and three representative examples of donor species were evaluated for their interactive behavior towards Zn(II), Cd(II) and Hg(II) ions in comparable reaction conditions. The, interactive behavior of Zn(II), Cd(II) and Hg(II) ions were entirely different from each other and allow one in observing three different trends for their reactivity patterns in similar environment. These study allow one to visualize the Hg(II) when it behaves like ‘hard’ Zn(II) or its individual performances being ‘soft’ in nature and

burdened with characteristic heavy metal effects. Therefore, it may be concluded that the behavior of these metal ions may be seriously influenced by the ligand architecture and position of heteroatoms in the donor species.

**Chapter IV** further elaborates the design and synthesis of a series of *Schiff-base* based acyclic organic donor species with ON<sub>2</sub>E<sub>2</sub> (E = S, Se or Te) donor combinations with structurally rigid phenolic (-OH) and imine (-C=N-) linkage with appended chalcogen bearing flexible donor arms. The chemistry of UO<sub>2</sub><sup>2+</sup> ion with these donor species was found remarkably interesting and discussed. The outcome of these results also form experimental basis in viewing the adventitious role of water and critical behavior of UO<sub>2</sub><sup>2+</sup> ion activity (as oxidizing, reducing or catalytic) may be relevant to many chemical, biological and environmental processes.

**Chapter V** describes the synthesis of N and S/Se substituted organic donor functionalities assisting the preorganized bowl shaped cyclotrimeratrylene (CTV) molecular architecture. These molecular species have shown '*homomeric inclusion*' phenomenon in which inclusion of one molecule into the cavity of other molecule with exactly similar architecture. Functionalization of these CTV derivatives with chalcogen donors has shown enhancement in their interactive ability towards guest species and formation of metallosupramolecular assembly with Ag(I) salts with nitrate or perchlorate as anions.

**Chapter VI** describes the synthesis of chalcogen assisted pillar[5]arene derivatives considering their potential as host species. The rigid pillar shaped structure and highly rich electron density in the cavity makes them selective host species towards long chain linear aliphatic guest molecules over their branched chain or cyclic analogues. The chalcogen functionalized pillar[5]arene derivatives have also shown their selectivity for iodide ion with respect to other competitive anions.

## सारांश

शोध प्रबंध शीर्षक "डिजाइन एंड सिंथेसिस ऑफ़ N- एंड S/Se- सब्स्टिट्यूटेड आर्गेनिक स्पीशीज एंड देयर एक्सेप्शनल बिहेवियर टुवर्ड्स  $d^{10}$  मेटल आयन्स,  $UO_2^{2+}$  आयन एंड आर्गेनिक गेस्ट मॉलीक्यूल्स" नए प्रकार के कार्बनिक हेटेरोएटम दाता प्रजातियों या चालकोजेन परमाणुओं को शामिल करके संशोधित किए गए आर्किटेक्चर के संश्लेषण का वर्णन करता है, जिसमें मुख्य रूप से सल्फर, नियंत्रित ज्यामितीय और दाता परमाणुओं की नई व्यवस्था के साथ  $d^{10}$  धातु आयनों,  $UO_2^{2+}$  आयन और कार्बनिक अतिथि अणुओं के प्रति उनके व्यवहार को समझने की चेष्टा की गयी है।

**अध्याय I** विविध अचक्रीय से लेकर चक्रीय एनालॉग पर विभिन्न हेटेरोएटम डोनर कॉम्बिनेशन वाले लिगेंड डिजाइन पहलुओं पर परिचयात्मक टिप्पणी करता है, और पिछले ढाई दशकों में विभिन्न क्षेत्रों में इसके संभावित अनुप्रयोगों के प्रारंभिक परिचयों पर भी प्रकाश डालता है। यह अध्याय वर्तमान शोध कार्यों के उद्देश्यों की भी व्याख्या करता है।

**अध्याय II** अनुसंधान कार्यों के दौरान उपयोग किए जाने वाले रसायनों और अभिकर्मकों की सूची प्रदान करता है और व्यावसायिक रूप से अनुपलब्ध शुरू करने वाली सामग्रियों की तैयारी के लिए अपनाई गई सिंथेटिक कार्यप्रणाली का विवरण भी प्रदान करता है। यह अध्याय नए संश्लेषित यौगिकों के लक्षण वर्णन के लिए उपयोग किए जाने वाले विभिन्न भौतिक-रासायनिक और स्पेक्ट्रोस्कोपिक अध्ययनों की भी व्याख्या करता है।

**अध्याय III** में 1,2,3- ट्रायजोळ आधारित अचक्रीय कार्बनिक दाताओं को विषम संरचनात्मक N, S/Se दाता संयोजनों को उनके संरचनात्मक ढांचे में प्रभावित करने वाले संश्लेषण के साथ संबंधित है और दाता प्रजातियों के तीन प्रतिनिधि उदाहरणों का मूल्यांकन  $Zn(II)$ ,  $Cd(II)$  और  $Hg(II)$  आयन के प्रति उनके संवादात्मक व्यवहार के लिए तुलनीय प्रतिक्रिया स्थितियों में किया गया था।  $Zn(II)$ ,  $Cd(II)$  और  $Hg(II)$  आयनों का संवादात्मक व्यवहार एक-दूसरे से पूरी तरह से अलग था और एक समान वातावरण में अपने

प्रतिक्रियात्मक स्वरूप के लिए तीन अलग-अलग रुझानों का अवलोकन करने की अनुमति देता है। ये अध्ययन हमें यह कल्पना करने की अनुमति देता है कि भारी धातु प्रभाव से बोझिल Hg (II) जो कि प्राकृतिक रूप से 'मुलायम' होता है परन्तु विभिन्न परिस्थितियों में 'कठोर' Zn (II) की तरह व्यवहार करने लगता है। इसलिए, यह निष्कर्ष निकाला जा सकता है कि इन धातु आयनों के व्यवहार को लिगेण्ड वास्तुकला और दाता प्रजातियों में हेटेरोएटम्स की स्थिति से गंभीरता से प्रभावित किया जा सकता है।

**अध्याय IV** ON<sub>2</sub>E<sub>2</sub> (E = S, Se या Te) डोनर संयोजनों के साथ संरचनात्मक रूप से कठोर फेनोलिक (-OH) और इमीन (-C=N-) लिंकेज के साथ चालकोजेन के साथ जुड़े लचीले दाता आर्म्स, शिफ-बेस आधारित अचक्रीय कार्बनिक दाता प्रजातियों की एक श्रृंखला के डिजाइन और संश्लेषण को विस्तृत करता है। इन दाता प्रजातियों के साथ UO<sub>2</sub><sup>2+</sup> आयन का रसायन विज्ञान उल्लेखनीय रूप से दिलचस्प पाया गया। इस अध्याय के परिणाम पानी की भूमिका और UO<sub>2</sub><sup>2+</sup> आयन गतिविधि के महत्वपूर्ण व्यवहार (ऑक्सीकरण के रूप में, ऑक्सीकरण को कम करने या उत्प्रेरक के रूप में) को देखने के लिए प्रयोगात्मक आधार बनाते हैं, तथा कई रासायनिक, जैविक और पर्यावरणीय प्रक्रियाओं के लिए प्रासंगिक हो सकते हैं।

**अध्याय V** में N और S/Se प्रतिस्थापित अकार्बनिक दाता के क्रियात्मकताओं के आधार पर जो पहले से संगठित कटोरे के आकार के साइक्लोट्राइवरेट्रीलीन (CTV) आणविक वास्तुकला के संश्लेषण के बारे में वर्णन किया गया है। इन आणविक प्रजातियों ने 'होमोमैरिक इंकलूजन' की घटना को दिखाया है जिसमें एक अणु को अन्य अणु के गुहा में बिल्कुल समान वास्तुकला के साथ शामिल किया गया है। चालकोजेन दाताओं के साथ इन सीटीवी डेरिवेटिव के कार्यात्मककरण ने अतिथि प्रजातियों के प्रति उनकी संवादात्मक क्षमता में वृद्धि को दिखाया है और Ag(I) लवण के साथ नाइट्रेट या परक्लोरेट के साथ आयनों के रूप में मेटालोसुपरामॉलीक्यूलर असेंबली का गठन किया है।

**अध्याय VI** में चालकोजेन से जुड़े पिलर[5]अरीन डेरिवेटिव्स के संश्लेषण का वर्णन है, तथा उनकी संभावित मेजबान प्रजातियों के रूप में उनकी क्षमता पर विचार करता है। कठोर स्तंभ के आकार की संरचना और गुहा में अत्यधिक समृद्ध इलेक्ट्रॉन घनत्व उन्हें अपनी शाखायुक्त श्रृंखला या चक्रीय एनालॉग्स पर लंबी श्रृंखला रेखीय स्निग्ध अतिथि अणुओं के लिए चयनात्मक मेजबान प्रजातियां बनाता है। चालकोजेन क्रियाशील पिलर[5]अरीन डेरिवेटिव ने अन्य प्रतिस्पर्धी आयनों के संबंध में आयोडाइड आयन के लिए अपनी चयनात्मकता भी दिखाई है।



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## Abbreviations used

THF	Tetrahydrofuran
TFA	Trifluoroacetic acid
HBr	Hydrobromic acid
DMF	Dimethylformamide
IR	Infrared
DIPEA	N,N-diisopropylethylamine
Hz	Hertz
MHz	Mega Hertz
h	Hour
g	Gram
M	Molar
mp	Melting point
equiv.	Equivalent
mmol	Millimole
Anal. calcd.	Analytically calculated
NMR	Nuclear magnetic resonance
mL	Millilitre
s	singlet
d	doublet
dd	double doublet
t	triplet
m	multiplet
br	broad
ppm	parts per million