

**STUDIES ON REACTIVITY AND MOLECULAR
STRUCTURES OF URANYL (VI) ION IN RESPONSE TO O,
N, S- BASED ACYCLIC AND CYCLIC ORGANIC SPECIES
IN NON-AQUEOUS MEDIUM**

JYOTI



**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
SEPTEMBER 2022**

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by

JYOTI

Submitted

In fulfilment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

to the



**DEPARTMENT OF CHEMISTRY
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SEPTEMBER 2022**

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Dedicated to

My

Supportive Teachers,

Angelic Parents, and Beloved Husband

CERTIFICATE

*This is to certify that the thesis entitled, “**Studies on Reactivity and Molecular Structures of Uranyl (VI) Ion in Response to O, N, S– based Acyclic and Cyclic Organic Species in Non–Aqueous Medium**” being submitted by **Ms. Jyoti**, to the **Indian Institute of Technology Delhi** for the award of degree of ‘**Doctor of Philosophy**’ in Chemistry is a bonafied research work carried out by her. Ms. Jyoti 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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Jyoti

ABSTRACT

The thesis entitled “***Studies on Reactivity and Molecular Structures of Uranyl (VI) Ion in Response to O, N, S– based Acyclic and Cyclic Organic Species in Non–Aqueous Medium***” deals with the study on UO_2^{2+} ion towards a series of acyclic and cyclic species bearing phenolic ($-\text{OH}$), ($-\text{HC}=\text{N}-$), ($-\text{C}=\text{O}$) and (O, N, S) groups as donor functionalities for evaluating its functional activity in non–aqueous medium. The thesis is divided into six chapters including general introduction on uranyl ion, materials and methods and the research findings are discussed in four chapters (III–VI).

Chapter I provides a key introduction to inorganic chemist’s evaluation of the behavior of uranyl (VI) ion in diverse environments including coordination chemistry, as well as the goals and objectives of the current research.

Chapter II provides the list of chemicals and reagents procured through various sources and details of the synthetic procedures adopted for the preparation of starting materials that are not commercially available. It also provides information about the physicochemical, spectroscopic, and crystallographic techniques used for the characterization of newly synthesized derivatives.

Chapter III discusses the behavior of UO_2^{2+} ion in geometrically constrained environment of di– and trianionic organic donor species derived from 2–hydroxyacetophenone and dialkyl –diamines, –triamines, –tetramines, alcohols, thio– and selenoethers. Coordinatively, UO_2^{2+} ion follow the classical pathways of coordination chemistry with donor species used herein forming mono and dinuclear complexes. The stability of the complexes in solution were found remarkable and thus, the donor species might prove interesting tools to evaluate their potential as an extractants for UO_2^{2+} ion in non–aqueous medium.

Chapter IV discusses the activities of UO_2^{2+} ion towards acyclic organic donor species bearing carbohydrazide or thio-carbohydrazide functionalities. This study is particularly interesting since the complexes have significantly different coordination geometries or ligand conformations than other oxo-metal (MoO_2^{2+} , VO_2^{2+}) cation complexes previously reported. Naturally, the behavior of UO_2^{2+} ion differs from that of other transition metal oxo-analogues. Nevertheless, these donor species are important in understanding the role of hydration water, in addition to the numerous parameters that determine the reactivity patterns of UO_2^{2+} species.

Chapter V discusses the functional activities of $\text{U}^{\text{VI}}\text{O}_2^{2+}$ ion with ($\text{O}_2\text{N}_2\text{S}_2$) type organic bases bearing ($-\text{OH}$), ($-\text{C}=\text{N}-$) and ($-\text{S}-$) donor functionalities. The UO_2^{2+} ion with these species revealed a unique bonding pattern, in particular, with intact $[\text{NO}_3]^-$ anion portion of the uranyl moiety. Indeed, isolation of the UO_2^{2+} ion from aqueous nitric media is a crucial step in *front-* and *back-* end of nuclear fuel cycle. The donor species may have the potential to be used in the separation process.

Chapter VI discusses the behavior of UO_2^{2+} ion towards cyclic azo-oxa and azo-thia crown ether type organic species with variable (O, N, S-) donor functionalities. Herein, two uranyl complexes of distinct anions (i.e., OCOCH_3 or NO_3) have been characterized by crystallographic methods. The donor species appeared to be in folded structure and therefore different behavior of UO_2^{2+} ion complexation with their respective anions is viable. The interaction of NO_3 or OCOCH_3 anions with UO_2^{2+} (VI) ions in reaction solvents is crucial and believed that under external influences they may provide the next advancement in structural complexities.

शोध प्रबंध का सार

गैर-जलीय माध्यम में ओ, एन, एस-आधारित अचक्रीय और चक्रीय कार्बनिक प्रजातियों के जवाब में यूरेनिल (VI) आयन की प्रतिक्रियाशीलता और आणविक संरचनाओं पर अध्ययन शीर्षक वाली थीसिस फेनोलिक (-OH), (-HC=N-), (-C=O) और (O, N, S) समूहों को दाता कार्यों के रूप में असर करने वाली अचक्रीय और चक्रीय प्रजातियों का यूरेनिल (VI) आयन की कार्यात्मक गतिविधि का मूल्यांकन करने के अध्ययन से संबंधित है। थीसिस को यूरेनिल आयन पर सामान्य परिचय सहित छह अध्यायों में विभाजित किया गया है, सामग्री और विधियों और शोध निष्कर्षों पर चार अध्यायों (III-VI) में चर्चा की गई है।

अध्याय I समन्वय रसायन शास्त्र सहित विभिन्न वातावरणों में यूरेनिल (VI) आयन के व्यवहार के साथ-साथ वर्तमान शोध के लक्ष्यों और उद्देश्यों के अकार्बनिक रसायनज्ञ के मूल्यांकन के लिए एक महत्वपूर्ण परिचय प्रदान करता है।

अध्याय II विभिन्न स्रोतों के माध्यम से प्राप्त रसायनों और अभिकर्मकों की सूची और व्यावसायिक रूप से उपलब्ध नहीं होने वाली प्रारंभिक सामग्री की तैयारी के लिए अपनाई गई कृत्रिम प्रक्रियाओं का विवरण प्रदान करता है। यह नए संश्लेषित डेरिवेटिव के लक्षण वर्णन के लिए उपयोग की जाने वाली भौतिक रासायनिक, स्पेक्ट्रोस्कोपिक और क्रिस्टलोग्राफिक तकनीकों के बारे में भी जानकारी प्रदान करता है।

अध्याय III 2-हाइड्रॉक्सीएसेटोफेनोन और डायलकिल-डायमाइन, -ट्रायमाइन, -टेट्रामाईंस, अल्कोहल, थियो- और सेलेनोएथर्स से प्राप्त डाय और त्रिकोणीय कार्बनिक दाता व्युत्पन्न प्रजाति के ज्यामितीय रूप से विवश वातावरण में यूरेनिल (VI) आयन के व्यवहार पर चर्चा करता है। समन्वित रूप से, यूरेनिल (VI) आयन, मोनो और द्वि-परमाणु जटिल बनाने वाली दाता प्रजातियों के साथ समन्वय रसायन विज्ञान के शास्त्रीय रास्ते का अनुसरण करते हैं। समाधान में परिसरों की स्थिरता उल्लेखनीय पाई गई और इस प्रकार, दाता प्रजातियां गैर-जलीय माध्यम में यूरेनिल (VI) आयन के लिए एक निकालने वाले के रूप में अपनी क्षमता का मूल्यांकन करने के लिए दिलचस्प उपकरण साबित हो सकती हैं।

अध्याय IV कार्बोहाइड्राजाइड या थियो-कार्बोहाइड्राजाइड कार्यात्मकताओं को प्रभावित करने वाली अचक्रीय कार्बनिक दाता प्रजातियों के प्रति यूरेनिल (VI) आयन की गतिविधियों पर चर्चा करता है। यह अध्ययन विशेष रूप से दिलचस्प है क्योंकि परिसरों में पहले से बताए गए अन्य ऑक्सो-धातु (MoO_2^{2+} , VO_2^{2+}) कटियन परिसरों की तुलना में काफी भिन्न समन्वय ज्यामिति या लिगेंड अनुरूपता है। स्वाभाविक रूप से, यूरेनिल (VI) आयन का व्यवहार अन्य संक्रमण धातु ऑक्सो-एनालॉग्स से भिन्न होता है। फिर भी, ये दाता प्रजातियां यूरेनिल (VI) प्रजातियों के प्रतिक्रियाशीलता पैटर्न को निर्धारित करने वाले कई मापदंडों के

अलावा, जलयोजन जल की भूमिका को समझने में महत्वपूर्ण हैं।

अध्याय V यूरेनिल (VI) आयन ($O_2N_2S_2$) प्रकार के कार्बनिक आधार असर ($-OH$), ($-C=N-$) और ($-S-$) दाता कार्यात्मकताओं के साथ कार्यात्मक गतिविधियों पर चर्चा करता है। इन प्रजातियों के साथ यूरेनिल (VI) आयन ने एक अद्वितीय बंधन पैटर्न का खुलासा किया, विशेष रूप से, बरकरार $[NO_3]^-$ यूरेनिल की मात्रा के आयन भाग के साथ। दरअसल, जलीय नाइट्रिक मीडिया से यूरेनिल (VI) आयन का अलगाव परमाणु ईंधन चक्र के आगे और पीछे के अंत में एक महत्वपूर्ण कदम है। दाता प्रजातियों में पृथक्करण प्रक्रिया में उपयोग किए जाने की क्षमता हो सकती है।

अध्याय VI चक्रीय एज़ो-ऑक्सा और एज़ो-थिया क्राउन ईथर प्रकार कार्बनिक प्रजातियों के प्रति यूरेनिल (VI) आयन के व्यवहार पर चर्चा (O, N, S) दाता कार्यात्मकताओं के साथ चर्चा करता है। इसके साथ ही, अलग-अलग आयनों (यानी, $OCOCH_3$ या NO_3) के दो यूरेनिल परिसरों को क्रिस्टलोग्राफिक तरीकों द्वारा चित्रित किया गया है। दाता प्रजाति मुड़ी हुई संरचना में प्रतीत होती है और इसलिए उनके संबंधित आयनों के साथ यूरेनिल (VI) आयन संकुलन का भिन्न व्यवहार व्यवहार्य है। प्रतिक्रिया सॉल्वेंट्स में यूरेनिल (VI) आयनों के साथ NO_3 या $OCOCH_3$ आयनों की बातचीत महत्वपूर्ण है और माना जाता है कि बाहरी प्रभावों के तहत वे संरचनात्मक जटिलताओं में अगली प्रगति प्रदान कर सकते हैं।

TABLE OF CONTENTS

| | | |
|----------------------------------|---|-----------|
| <i>Certificate</i> | | i |
| <i>Acknowledgments</i> | | ii |
| <i>Abstract</i> | | iv |
| <i>List of Schemes</i> | | xii |
| <i>List of Figures</i> | | xiv |
| <i>List of Tables</i> | | xxi |
| <i>Abbreviations used</i> | | xxiii |
| Chapter I | GENERAL INTRODUCTION | 1 |
| | ❖ Introduction | 2 |
| | ❖ References | 32 |
| Chapter II | MATERIALS AND METHODS | 42 |
| | ❖ Chemicals used | 43 |
| | ❖ Synthesis of Precursors | 44 |
| | ❖ Physicochemical Studies | 49 |
| | ❖ References | 52 |
| Chapter III | Behavior of UO_2^{2+} Ion in Geometrically Constrained Environment of Di- and Trianionic Organic Donor Species Derived from 2-hydroxyacetophenone and Dialkyl -Diamines, -Triamines, -Tetramines, Alcohols, Thio- and Selenoethers | 54 |
| | ❖ Abstract | 55 |
| | ❖ Introduction | 55 |
| | ❖ Results and Discussion | 57–79 |
| | • Synthesis of acyclic donor species (H_2L_1 – H_2L_8) | |
| | • Physicochemical and spectral studies of species (H_2L_1 – H_2L_8) and their uranyl | |

| | |
|--|----|
| complexes (C ₁ and C ₂) | |
| ▪ Elemental Analysis | |
| ▪ Mass Spectrometry Studies | |
| ▪ ¹ H NMR Studies | |
| ▪ ¹³ C{ ¹ H} NMR Studies | |
| • Solution State Studies | |
| ▪ UV–Vis. Spectroscopic Studies | |
| ▪ Fluorescence Studies | |
| • Complexation Studies | |
| • IR Studies | |
| • ESI–MS of Complex (C ₁) | |
| • Single Crystal X–ray Diffraction Studies | |
| ❖ Conclusion | 79 |
| ❖ Experimental Section | 80 |
| ❖ Tables | 85 |
| ❖ References | 88 |

Chapter IV Activities of UO₂²⁺ Ion Towards Acyclic Organic Donor Species Bearing Carbohydrazide or Thio–carbohydrazide Functionalities 92

| | |
|---|--------|
| ❖ Abstract | 93 |
| ❖ Introduction | 93 |
| ❖ Results and Discussion | 95–120 |
| • Synthesis of carbohydrazide/thio–carbohydrazide based donor Species (L ₁ –L ₁₂) | |
| • Physicochemical and spectral studies of species (L ₁ –L ₁₂) and their uranyl complexes (C ₁ –C ₅) | |
| ▪ Elemental Analysis | |
| ▪ Mass Spectrometry Studies | |
| ▪ ¹ H NMR Studies | |
| ▪ ¹³ C{ ¹ H} NMR Studies | |
| • Solution Studies | |

| | |
|--|-----|
| <ul style="list-style-type: none"> ▪ ^1H NMR titration experiments ▪ UV–Vis. Spectroscopic Studies ▪ Fluorescence Studies | |
| • Complexation Studies | |
| • IR Studies | |
| • ESI–MS of Complexes (C_2 and C_3) | |
| • Single Crystal X–ray Diffraction Studies | |
| ❖ Conclusion | 120 |
| ❖ Experimental Section | 121 |
| ❖ Tables | 128 |
| ❖ References | 137 |

Chapter V Functional Activities of $\text{U}^{\text{VI}}\text{O}_2^{2+}$ Ion with ($\text{O}_2\text{N}_2\text{S}_2$) type Organic bases bearing ($-\text{OH}$), ($-\text{C}=\text{N}-$) and ($-\text{S}-$) Donor Functionalities

| | |
|--|------------|
| Functionalities | 140 |
| ❖ Abstract | 141 |
| ❖ Introduction | 141 |
| ❖ Results and Discussion | 142–161 |
| <ul style="list-style-type: none"> • Synthesis of acyclic organic species featuring ($\text{O}_2\text{N}_2\text{S}_2$) donor heteroatoms ($\text{H}_2\text{L}_1-\text{H}_2\text{L}_{10}$) • Physicochemical and spectral studies of species ($\text{H}_2\text{L}_1-\text{H}_2\text{L}_{10}$) and their uranyl complexes (C_1 and C_{10}) <ul style="list-style-type: none"> ▪ Elemental Analysis ▪ Mass Spectrometry Studies ▪ ^1H NMR Studies ▪ $^{13}\text{C}\{^1\text{H}\}$ NMR Studies • Solution Studies <ul style="list-style-type: none"> ▪ UV–Vis. Spectroscopic Studies ▪ Fluorescence Studies • Complexation Studies • IR Studies • ESI–MS of Complexes (C_1 and C_{10}) | |

| | | |
|-------------------|--|------------|
| | • Single Crystal X–ray Diffraction Studies | |
| ❖ | Conclusion | 162 |
| ❖ | Experimental Section | 163 |
| ❖ | Tables | 169 |
| ❖ | References | 171 |
| Chapter VI | Behavior of UO_2^{2+} Ion Towards Cyclic Azo–oxa and Azo–thia Crown Ether Type Organic Species with Variable (O, N, S–) Donor Functionalities | 174 |
| ❖ | Abstract | 175 |
| ❖ | Introduction | 175 |
| ❖ | Results and Discussion | 176–194 |
| | • Synthesis of cyclic donor species (L ₁ –L ₇) | |
| | • Physicochemical and spectral studies of cyclic species (L ₁ –L ₇) and their uranyl complexes (C ₁ and C ₂) | |
| | ▪ Elemental Analysis | |
| | ▪ Mass Spectrometry Studies | |
| | ▪ ¹ H NMR Studies | |
| | ▪ ¹³ C{ ¹ H} NMR Studies | |
| | • Solution Studies | |
| | ▪ UV–Vis. Spectroscopic Studies | |
| | ▪ Fluorescence Studies | |
| | • Complexation Studies | |
| | • IR Studies | |
| | • Single Crystal X–ray Diffraction Studies | |
| ❖ | Conclusion | 194 |
| ❖ | Experimental Section | 195 |
| ❖ | Tables | 199 |
| ❖ | References | 202 |
| BIO-DATA | | 206 |

LIST OF SCHEMES

Chapter I

| Scheme no. | Scheme Caption | Page no. |
|------------|--|----------|
| 1.1 | Precipitation of a crystalline complex $(\text{UO}_2)(adam)_2(\text{NO}_3)_2 \cdot 2(adam)$ from aqueous HNO_3 (0.5 M). | 15 |
| 1.2 | Dinuclear $[(\text{UO}_2)_2(\text{L})_2]$ formation displaying the HL(Ac) atom numbering. | 16 |
| 1.3 | Proposed formation of $[(\text{UO}_2)_3(\mu_3\text{-O})(\text{L})_3]^{2-}$ from $[(\text{UO}_2)_2(\text{L})_2]$ via coordination of one water molecule, followed by stepwise double deprotonation. | 16 |
| 1.4 | Synthesis of O, N, S-based donor species (L_1) and its interaction mechanism with UO_2^{2+} salts. | 17 |
| 1.5 | Uranyl containing complexes exhibiting $\text{O}=\text{U}=\text{O} \rightarrow \text{M}$ interactions. | 19 |

Chapter II

| Scheme no. | Scheme Caption | Page no. |
|------------|---|----------|
| 2.1 | Synthetic scheme for the synthesis of 2,2'-thiodiethanamine. | 45 |
| 2.2 | Synthetic scheme for the synthesis of 2,2'-selenodiethanamine. | 45 |
| 2.3 | Synthetic scheme for the synthesis of 1,2-bis(2-aminophenylthio)ethane. | 46 |
| 2.4 | Synthetic scheme for the synthesis of 1,2-bis(2-aminoethylthio)ethane. | 47 |
| 2.5 | Synthetic scheme for the synthesis of 2,6-diformyl-4-methylphenol. | 47 |
| 2.6 | Synthetic scheme for the synthesis of 2,6-diformylpyridine. | 48 |

Chapter III

| Scheme no. | Scheme Caption | Page no. |
|------------|---|----------|
| 3.1 | Experimental procedure for the synthesis of the donor species ($\text{H}_2\text{L}_1\text{-H}_2\text{L}_8$). | 57 |
| 3.2 | Complexation reactions of donor species and UO_2^{2+} ion at room temperature and shown structures on the basis of their X-ray | 71 |

| | | |
|--|-----------|--|
| | analysis. | |
|--|-----------|--|

Chapter IV

| Scheme no. | Scheme Caption | Page no. |
|------------|--|----------|
| 4.1 | Experimental route for the synthesis of donor species (H_2L_1 and H_2L_2). | 95 |
| 4.2 | Complexation reactions of donor species and UO_2^{2+} ion at room temperature and shown structures on the basis of their X-ray analysis. | 107 |

Chapter V

| Scheme no. | Scheme Caption | Page no. |
|------------|--|----------|
| 5.1 | Synthetic scheme for the preparation of ($O_2N_2S_2$) type acyclic donor species ($H_2L_1-H_2L_{10}$). | 143 |
| 5.2 | Complexation reactions of donor species and UO_2^{2+} ion at room temperature and shown structures on the basis of their X-ray analysis. | 155 |

Chapter VI

| Scheme no. | Scheme Caption | Page no. |
|------------|--|----------|
| 6.1 | Experimental procedure for the synthesis of the donor species (L_1-L_7). | 177 |
| 6.2 | Complexation reactions of donor species and UO_2^{2+} ion at room temperature and shown structures on the basis of their X-ray analysis. | 188 |

LIST OF FIGURES

Chapter I

| Figure no. | Figure Caption | Page no. |
|------------|--|----------|
| 1.1 | Formation of high-nuclearity complexes <i>via</i> . bridging oxo- and hydroxo- groups from the hydrolysis of the U(VI) cation. | 9 |
| 1.2 | Possible hydrolyzed species obtained potentiometrically. | 10 |
| 1.3 | X-ray illustration of the structure $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. | 13 |
| 1.4 | <i>Cis</i> , <i>trans</i> -conformations of uranyl nitrate in presence of donor species | 14 |
| 1.5 | (a) Complete encapsulation of the UO_2^{2+} ion, and (b) second-sphere hydrogen-bonded complex of UO_2^{2+} ion. | 18 |
| 1.6 | Photoinduced transformation of uranyl nitrate 18-Crown-6-ether complex in nonaqueous medium. | 19 |
| 1.7 | $[\{\{\text{UO}_2(\text{salen})\}_2\text{Mn}(\text{Py})_3\}_6]$, a dodecanuclear uranyl(V) complex, a wheel type structure, containing six manganese(II) centres. | 21 |
| 1.8 | UO_2^{2+} template condensation of 1,2-dicyanobenzene and influence of water. | 23 |
| 1.9 | Application of pentadentate bis-phosphonated pyridine as uranyl decorporation agent. | 25 |
| 1.10 | Potential application of Hinokitil or Hino in chelation therapy. | 26 |

Chapter III

| Figure no. | Figure Caption | Page no. |
|------------|---|----------|
| 3.1 | ESI-MS spectra of species H_2L_1 and H_3L_2 showing fragmentation patterns and molecular ion peak. | 59 |
| 3.2 | ^1H NMR spectrum of species H_2L_1 (in CDCl_3) with assignments of proton signals. | 60 |
| 3.3 | ^1H NMR spectrum of the donor species H_3L_2 (in $\text{DMSO}-d_6$) with corresponding assignable proton signals. | 61 |
| 3.4 | $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of species H_2L_1 in CDCl_3 . | 62 |
| 3.5 | $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of species H_3L_2 in $(\text{DMSO}-d_6)$. | 62 |
| 3.6 | Concentration-dependent absorption spectra of (a) species H_2L_1 | 63 |

| | | |
|------|--|----|
| | and (b) H_3L_2 in CH_3CN . | |
| 3.7 | Spectrophotometric UV–Vis. titrations: (a) spectroscopic changes titrating species H_2L_1 (1×10^{-4} M) with $\text{UO}_2(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$ (1×10^{-3} M) or $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1×10^{-3} M) in CH_3CN to a (UO_2^{2+} : H_2L_1) (1:1) molar ratio, (b) spectroscopic changes upon titrating species H_2L_1 (1×10^{-4} M) with $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1×10^{-3} M) in CH_3CN starting from (UO_2^{2+} : H_2L_1) molar concentration (0.1:1) up to (2:1). | 64 |
| 3.8 | Spectrophotometric UV–Vis. titrations: (a) spectroscopic changes titrating species H_3L_2 (1×10^{-4} M) with $\text{UO}_2(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$ (1×10^{-3} M) in CH_3CN and (b) spectroscopic changes titrating species H_3L_2 (1×10^{-4} M) with $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1×10^{-3} M) in CH_3CN starting from (UO_2^{2+} : H_3L_2) molar concentration (0.1:1) up to (2:1). | 66 |
| 3.9 | Spectrophotometric UV–Vis. titrations: (a) spectroscopic changes titrating species H_2L_6 (1×10^{-5} M) with $\text{UO}_2(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$ (1×10^{-3} M) in CH_3CN and (b) spectroscopic changes titrating species H_2L_6 (1×10^{-5} M) with $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1×10^{-3} M) in CH_3CN starting from (UO_2^{2+} : H_2L_6) molar concentration (0.1:1) up to (2:1). | 67 |
| 3.10 | Spectrophotometric UV–Vis. titrations: (a) spectroscopic changes titrating species H_2L_7 (1×10^{-4} M) with $\text{UO}_2(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$ (1×10^{-3} M) in CH_3CN and (b) spectroscopic changes titrating species H_2L_7 (1×10^{-4} M) with $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1×10^{-3} M) in CH_3CN starting from (UO_2^{2+} : H_2L_7) molar concentration (0.1:1) up to (2:1). | 68 |
| 3.11 | Fluorescence spectral changes upon successive addition of a solution of UO_2^{2+} ion to a solution of (a) species H_2L_1 (1×10^{-4} M) ($\lambda_{\text{Ex.}} = 350$ nm, $\lambda_{\text{Em.}} = 370$ nm) as $\text{UO}_2(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$ (1×10^{-3} M) in CH_3CN , (b) species H_2L_1 (1×10^{-4} M) ($\lambda_{\text{Ex.}} = 350$ nm, $\lambda_{\text{Em.}} = 370$ nm) as $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1×10^{-3} M) in CH_3CN , (c) species H_3L_2 (1×10^{-4} M) ($\lambda_{\text{Ex.}} = 350$ nm, $\lambda_{\text{Em.}} = 370$ nm) as $\text{UO}_2(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$ (1×10^{-3} M) in CH_3CN and (d) species H_3L_2 (1×10^{-4} M) ($\lambda_{\text{Ex.}} = 350$ nm, $\lambda_{\text{Em.}} = 370$ nm) as $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1×10^{-3} M) in CH_3CN starting from (UO_2^{2+} : L) (1:1) molar concentration up to (5:1). | 69 |
| 3.12 | Fluorescence spectral changes upon successive addition of a solution of UO_2^{2+} ion to a solution of (e) species H_2L_6 (1×10^{-5} M) ($\lambda_{\text{Ex.}} = 340$ nm, $\lambda_{\text{Em.}} = 360$ nm) as $\text{UO}_2(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$ (1×10^{-3} M) in CH_3CN , (f) species H_2L_6 (1×10^{-5} M) ($\lambda_{\text{Ex.}} = 340$ nm, $\lambda_{\text{Em.}} = 360$ nm) as $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1×10^{-3} M) in CH_3CN , (g) species H_2L_7 (1×10^{-4} M) ($\lambda_{\text{Ex.}} = 340$ nm, $\lambda_{\text{Em.}} = 360$ nm) as $\text{UO}_2(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$ (1×10^{-3} M) in CH_3CN , and (h) species H_2L_7 (1×10^{-4} M) ($\lambda_{\text{Ex.}} = 340$ nm, $\lambda_{\text{Em.}} = 360$ nm) as $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1×10^{-3} M) in CH_3CN starting from UO_2^{2+} : L (1:1) molar concentration up to (5:1). | 70 |
| 3.13 | Overlay of the IR spectra of (H_2L_1) (blue) and its complex with $\text{UO}_2(\text{NO}_3)_2$ (red) exhibiting ($\text{UO}_2^{2+} \leftarrow \text{H}_2\text{L}_1$) coordination. | 72 |

| | | |
|------|--|-------|
| 3.14 | Overlay of the IR spectra of (H₃L₂) (green) and its complex with UO ₂ (NO ₃) ₂ (pink) exhibiting (UO ₂ ²⁺ ← H ₃ L ₂) coordination. | 72 |
| 3.15 | ESI–MS spectrum of uranyl complex species (C₁). | 74 |
| 3.16 | (a) Perspective view of species H₂L₆ showing the atom numbering scheme with ellipsoids represent thermal parameters at the 50% probability level and (b) showing intramolecular H–bonding interactions. | 75 |
| 3.17 | (a) Perspective view of 5–coordinated mononuclear uranyl complex species C₁ showing the atom numbering scheme with ellipsoids represent thermal parameters at the 50% probability level (b) packing view of mononuclear uranyl complex species C₁ showing weak interactions. | 76–77 |
| 3.18 | (a) Perspective view of 5–coordinated dinuclear uranyl complex species C₂ showing the atomic numbering scheme with ellipsoids represent thermal parameters at the 50% probability level and (b) showing intermolecular H–bonding interactions. | 78 |

Chapter IV

| Figure no. | Figure Caption | Page no. |
|------------|--|----------|
| 4.1 | ESI–MS spectra of species L₂ and L₄ showing fragmentation patterns and molecular ion peak. | 97 |
| 4.2 | ¹ H NMR spectrum of the species L₂ (in DMSO–d ₆). | 98 |
| 4.3 | ¹³ C{ ¹ H} NMR spectrum of species L₂ in (DMSO–d ₆). | 99 |
| 4.4 | Spectral changes observed in ¹ H NMR on titrating species L₂ with UO ₂ (OCOCH ₃) ₂ •2H ₂ O in DMSO–d ₆ (up to UO ₂ ²⁺ : L₂ ratio reached 0.1:1 to 1.2:1). Peak 'a' and 'b' correspond to phenolic and imine proton (–CH=N–) of donor species L₂ . | 100 |
| 4.5 | Concentration–dependent absorption spectra of (a) species L₁ and (b) species L₂ in CH ₃ CN. | 101 |
| 4.6 | Spectrophotometric UV–Vis. titrations: (a) spectroscopic changes titrating species L₁ (1 x 10 ^{–5} M) with UO ₂ (OCOCH ₃) ₂ •2H ₂ O (1 x 10 ^{–3} M) in CH ₃ CN and (b) spectroscopic changes titrating species L₁ (1 x 10 ^{–5} M) with UO ₂ (NO ₃) ₂ •6H ₂ O (1 x 10 ^{–3} M) in CH ₃ CN starting from (UO ₂ ²⁺ : L₁) molar concentration (0.1:1) up to (2:1). | 102 |
| 4.7 | Spectrophotometric UV–Vis. titrations: (a) spectroscopic changes titrating species L₂ (1 x 10 ^{–5} M) with UO ₂ (OCOCH ₃) ₂ •2H ₂ O (1 x 10 ^{–3} M) in CH ₃ CN and (b) spectroscopic changes titrating species L₂ (1 x 10 ^{–5} M) with UO ₂ (NO ₃) ₂ •6H ₂ O (1 x 10 ^{–3} M) in CH ₃ CN starting | 103 |

| | | |
|------|--|-----|
| | from (UO ₂ ²⁺ : L ₂) molar concentration (0.1:1) up to (2:1). | |
| 4.8 | Spectrophotometric UV–Vis. titrations: (a) spectroscopic changes titrating species L ₃ (1 x 10 ⁻⁵ M) with UO ₂ (OCOCH ₃) ₂ •2H ₂ O (1 x 10 ⁻³ M) in CH ₃ CN and (b) spectroscopic changes titrating species L ₃ (1 x 10 ⁻⁵ M) with UO ₂ (NO ₃) ₂ •6H ₂ O (1 x 10 ⁻³ M) in CH ₃ CN starting from (UO ₂ ²⁺ : L ₃) molar concentration (0.1:1) up to (2:1). | 104 |
| 4.9 | Fluorescence spectral changes upon successive addition of a solution of UO ₂ ²⁺ ion to a solution of (a) species L ₁ (1 x 10 ⁻⁵ M) (λ _{Ex.} = 380 nm, λ _{Em.} = 400 nm) as UO ₂ (OCOCH ₃) ₂ •2H ₂ O (1 x 10 ⁻³ M) in CH ₃ CN, (b) species L ₁ (1 x 10 ⁻⁵ M) (λ _{Ex.} = 380 nm, λ _{Em.} = 400 nm) as UO ₂ (NO ₃) ₂ •6H ₂ O (1 x 10 ⁻³ M) in CH ₃ CN, (c) species L ₂ (1 x 10 ⁻⁵ M) (λ _{Ex.} = 340 nm, λ _{Em.} = 360 nm) as UO ₂ (OCOCH ₃) ₂ •2H ₂ O (1 x 10 ⁻³ M) in CH ₃ CN, (d) species L ₂ (1 x 10 ⁻⁵ M) (λ _{Ex.} = 340 nm, λ _{Em.} = 360 nm) as UO ₂ (NO ₃) ₂ •6H ₂ O (1 x 10 ⁻³ M) in CH ₃ CN, (e) species L ₃ (1 x 10 ⁻⁵ M) (λ _{Ex.} = 340 nm, λ _{Em.} = 385 nm) as UO ₂ (OCOCH ₃) ₂ •2H ₂ O (1 x 10 ⁻³ M) in CH ₃ CN and (f) species L ₃ (1 x 10 ⁻⁵ M) (λ _{Ex.} = 340 nm, λ _{Em.} = 385 nm) as UO ₂ (NO ₃) ₂ •6H ₂ O (1 x 10 ⁻³ M) in CH ₃ CN starting from (UO ₂ ²⁺ : L) (1:1) molar concentration up to (5:1). | 106 |
| 4.10 | Overlay of the IR spectra of (L ₁) (orange) and its complex with UO ₂ (OCOCH ₃) ₂ •2H ₂ O (purple) exhibiting (UO ₂ ²⁺ ← L ₁) coordination. | 108 |
| 4.11 | Overlay of the IR spectra of (L ₂) (red) and its complex with UO ₂ (OCOCH ₃) ₂ •2H ₂ O (green) exhibiting (UO ₂ ²⁺ ← L ₂) coordination. | 108 |
| 4.12 | Overlay of the IR spectra of (L ₃) (blue) and its complex with UO ₂ (OCOCH ₃) ₂ •2H ₂ O (red) exhibiting (UO ₂ ²⁺ ← L ₃) coordination. | 109 |
| 4.13 | ESI–MS spectrum of uranyl complex species (C ₂). | 110 |
| 4.14 | ESI–MS spectrum of uranyl complex species (C ₃). | 111 |
| 4.15 | Perspective view of species L ₁ showing the atom numbering scheme with ellipsoids represent thermal parameters at the 50% probability level. | 112 |
| 4.16 | Perspective view of species L ₃ showing the atom numbering scheme with ellipsoids represent thermal parameters at the 50% probability level. | 112 |
| 4.17 | Packing diagrams of (a) Species L ₁ showing intra– and intermolecular H–bonding and (b) Species L ₃ showing the water molecule entrapped between the two molecules with H–bonding. | 113 |
| 4.18 | Perspective view of 5–coordinated mononuclear uranyl complex species C ₁ showing the atom numbering scheme with ellipsoids represent thermal parameters at the 50% probability level. | 114 |

| | | |
|------|--|-----|
| 4.19 | Perspective view of 5–coordinated (a) expected dinuclear uranyl complex species C_(2a) and (b) unexpected dinuclear uranyl complex species C_(2b) showing the atom numbering scheme with ellipsoids represent thermal parameters at the 50% probability level. | 116 |
| 4.20 | Perspective view of 5–coordinated expected dinuclear uranyl complex species C₃ showing the atom numbering scheme with ellipsoids represent thermal parameters at the 50% probability level. | 117 |
| 4.21 | Perspective view of 5–coordinated unexpected dinuclear uranyl complex species C₄ showing the atom numbering scheme with ellipsoids represent thermal parameters at the 50% probability level. | 118 |
| 4.22 | Perspective view of 5–coordinated dinuclear uranyl complex species C₅ showing the atom numbering scheme with ellipsoids represent thermal parameters at the 50% probability level. | 119 |

Chapter V

| Figure no. | Figure Caption | Page no. |
|------------|---|----------|
| 5.1 | ESI–MS spectra of species H₂L₁ and H₂L₁₀ showing fragmentation with the molecular ion peak in desired isotopic pattern due to sulfur.[*Sulfur (¹⁶ S) has four stable isotopes: ³² S (95.02%), ³³ S (0.75%), ³⁴ S (4.21%), and ³⁶ S (0.02%)]. | 145 |
| 5.2 | ¹ H NMR spectrum of species H₂L₁ (in DMSO–d ₆). | 146 |
| 5.3 | ¹ H NMR spectrum of species H₂L₁₀ (in CDCl ₃) with corresponding proton signals. | 147 |
| 5.4 | ¹³ C{ ¹ H} NMR spectrum of species H₂L₁ in (DMSO–d ₆). | 148 |
| 5.5 | ¹³ C{ ¹ H} NMR spectrum of species H₂L₁₀ in CDCl ₃ . | 148 |
| 5.6 | Concentration–dependent absorption spectra of (a) species H₂L₁ and (b) species H₂L₁₀ (in CH ₃ CN). | 150 |
| 5.7 | Spectrophotometric UV–Vis. titrations: (a) spectroscopic changes titrating species H₂L₁ (1 x 10 ^{–4} M) with UO ₂ (OCOCH ₃) ₂ •2H ₂ O (1 x 10 ^{–3} M) or UO ₂ (NO ₃) ₂ •6H ₂ O (1 x 10 ^{–3} M) in CH ₃ CN to a molar (UO ₂ ²⁺ : H ₂ L ₁) (1:1) ratio, (b) spectroscopic changes titrating species H₂L₁ (1 x 10 ^{–4} M) with UO ₂ (NO ₃) ₂ •6H ₂ O (1 x 10 ^{–3} M) in CH ₃ CN starting from (UO ₂ ²⁺ : H ₂ L ₁) molar concentration (0.1:1) up to (2:1). | 151 |
| 5.8 | Spectrophotometric UV–Vis. titrations: (a) spectroscopic changes titrating species H₂L₁₀ (1 x 10 ^{–5} M) with UO ₂ (NO ₃) ₂ •6H ₂ O (1 x 10 ^{–3} | 152 |

| | | |
|------|---|-----|
| | M) in CH ₃ CN and (b) spectroscopic changes titrating species H₂L₁₀ (1 x 10 ⁻⁵ M) with UO ₂ (OCOCH ₃) ₂ •2H ₂ O (1 x 10 ⁻³ M) in CH ₃ CN starting from (UO ₂ ²⁺ : H ₂ L ₁₀) molar concentration (0.1:1) up to (2:1). | |
| 5.9 | Fluorescence spectral changes upon successive addition of a solution of UO ₂ ²⁺ ion to a solution of (a) species H₂L₁ (1 x 10 ⁻⁴ M) (λ _{Ex.} = 360 nm, λ _{Em.} = 380 nm) as UO ₂ (OCOCH ₃) ₂ •2H ₂ O (1 x 10 ⁻³ M) in CH ₃ CN, (b) species H₂L₁ (1 x 10 ⁻⁴ M) (λ _{Ex.} = 360 nm, λ _{Em.} = 380 nm) as UO ₂ (NO ₃) ₂ •6H ₂ O (1 x 10 ⁻³ M) in CH ₃ CN, (c) species H₂L₁₀ (1 x 10 ⁻⁵ M) (λ _{Ex.} = 340 nm, λ _{Em.} = 360 nm) as UO ₂ (OCOCH ₃) ₂ •2H ₂ O (1 x 10 ⁻³ M,) in CH ₃ CN and (d) species H₂L₁₀ (1x 10 ⁻⁵ M) (λ _{Ex.} = 340 nm, λ _{Em.} = 360 nm) as UO ₂ (NO ₃) ₂ •6H ₂ O (1 x 10 ⁻³ M) in CH ₃ CN starting from (UO ₂ ²⁺ : L) molar concentration (1:1) up to (5:1) ratio. | 153 |
| 5.10 | Overlay of the IR spectra of (H₂L₁) (purple) and its complex with UO ₂ (NO ₃) ₂ (green) exhibiting (UO ₂ ²⁺ ← H ₂ L ₁) coordination. | 156 |
| 5.11 | Overlay of the IR spectra of (H₂L₁₀) (teal blue) and its complex with UO ₂ (NO ₃) ₂ (orange) exhibiting (UO ₂ ²⁺ ← H ₂ L ₁₀) coordination. | 157 |
| 5.12 | ESI–MS spectra of uranyl complexes (C₁ and C₁₀). | 158 |
| 5.13 | Perspective view of 6–coordinated mononuclear uranyl complex (C₁) showing the atom numbering scheme with ellipsoids represent thermal parameters at the 30% probability level. | 159 |
| 5.14 | Packing view of mononuclear uranyl complex species (C₁) showing intermolecular H–bonding interactions. | 160 |
| 5.15 | Perspective view of 6–coordinated uranyl nitrate showing the atom numbering scheme with ellipsoids represent thermal parameters at the 50% probability level. | 161 |
| 5.16 | Perspective views of (a) species (C₁) showing <i>cis</i> –nitrate anions intersecting by planes and (b) uranyl nitrate showing both the <i>trans</i> –nitrate anions intersected by a single plane. | 161 |

Chapter VI

| Figure no. | Figure Caption | Page no. |
|------------|--|----------|
| 6.1 | ESI–MS spectra of species L₁ and L₆ showing fragmentation with the molecular ion peak in desired isotopic pattern. [*Sulfur (¹⁶ S) has four stable isotopes: ³² S (95.02%), ³³ S (0.75%), ³⁴ S (4.21%), and ³⁶ S (0.02%)]. | 179 |
| 6.2 | ¹ H NMR spectrum of species L₁ (in CDCl ₃) with the assignment of their corresponding proton signals. | 180 |
| 6.3 | ¹³ C{ ¹ H} NMR spectrum of species L₁ in CDCl ₃ . | 181 |

| | | |
|------|---|-----|
| 6.4 | Concentration-dependent absorption spectra for (a) species L₁ and (b) species L₂ in CH ₃ CN. | 182 |
| 6.5 | Spectrophotometric UV-Vis. titrations: (a) spectroscopic changes titrating species L₁ (1×10^{-4} M) with UO ₂ (OCOCH ₃) ₂ •2H ₂ O (1×10^{-3} M) in CH ₃ CN and (b) spectroscopic changes titrating species L₁ (1×10^{-4} M) with UO ₂ (NO ₃) ₂ •6H ₂ O (1×10^{-3} M) in CH ₃ CN, starting from (UO ₂ ²⁺ :L ₁) molar concentration (0.1:1) up to (2:1). | 183 |
| 6.6 | Spectrophotometric UV-Vis. titrations: (a) spectroscopic changes titrating species L₂ (1×10^{-5} M) with UO ₂ (OCOCH ₃) ₂ •2H ₂ O (1×10^{-3} M) in CH ₃ CN and (b) spectroscopic changes titrating species L₂ (1×10^{-5} M) with UO ₂ (NO ₃) ₂ •6H ₂ O (1×10^{-3} M) in CH ₃ CN, starting from (UO ₂ ²⁺ :L ₂) molar concentration (0.1:1) up to (2:1). | 185 |
| 6.7 | Fluorescence spectral changes upon successive addition of a solution of UO ₂ ²⁺ ion to a solution of (a) species L₁ (1×10^{-4} M) ($\lambda_{\text{Ex.}} = 370$ nm, $\lambda_{\text{Em.}} = 390$ nm) as UO ₂ (OCOCH ₃) ₂ •2H ₂ O (1×10^{-3} M) in CH ₃ CN, (b) species L₁ (1×10^{-4} M) ($\lambda_{\text{Ex.}} = 370$ nm, $\lambda_{\text{Em.}} = 390$ nm) as UO ₂ (NO ₃) ₂ •6H ₂ O (1×10^{-3} M) in CH ₃ CN, (c) species L₂ (1×10^{-5} M, ACN) ($\lambda_{\text{Ex.}} = 300$ nm, $\lambda_{\text{Em.}} = 320$ nm) as UO ₂ (OCOCH ₃) ₂ •2H ₂ O (1×10^{-3} M) in CH ₃ CN and (d) species L₂ (1×10^{-5} M) ($\lambda_{\text{Ex.}} = 300$ nm, $\lambda_{\text{Em.}} = 320$ nm) as UO ₂ (NO ₃) ₂ •6H ₂ O (1×10^{-3} M) in CH ₃ CN starting from (UO ₂ ²⁺ :L) molar concentration (1:1) up to (5:1). | 186 |
| 6.8 | Overlay of the IR spectra of (L₁) (orange) and its complex with UO ₂ (OCOCH ₃) ₂ •2H ₂ O (blue) exhibiting (UO ₂ ²⁺ ← L ₁) coordination. | 189 |
| 6.9 | Overlay of the IR spectra of (L₁) (orange) and its complex with UO ₂ (NO ₃) ₂ •6H ₂ O (green) exhibiting (UO ₂ ²⁺ ← L ₁) coordination. | 189 |
| 6.10 | ESI-MS spectra of uranyl complexes (C₁ and C₂). | 190 |
| 6.11 | Perspective views of 5-coordinated dinuclear uranyl complex species C₁ (a) front view and (b) top view showing the atom numbering scheme with ellipsoids at the 40% probability level. | 192 |
| 6.12 | Perspective view of 6-coordinated complex species C₂ as a dinuclear uranyl species (including H-bonding) showing the atom numbering scheme with ellipsoids at the 40% probability level. | 193 |
| 6.13 | Packing view of dinuclear uranyl complex species C₂ showing intermolecular H-bonding interactions. | 194 |

LIST OF TABLES

Chapter I

| Table no. | Title of the table | Page no. |
|-----------|--|----------|
| 1.1 | Ionic radii of U in various oxidation states and actinide elements (Ac–Lr) in their common oxidation states. | 4 |

Chapter III

| Table no. | Title of the table | Page no. |
|-----------|---|----------|
| 3.1 | Crystal data and refinement details for complexes C ₁ and C ₂ . | 85 |
| 3.2 | Selected bond lengths (Å) and bond angles (°) for C ₁ . | 86 |
| 3.3 | Selected bond lengths (Å) and bond angles (°) for C ₂ . | 87 |

Chapter IV

| Table no. | Title of the table | Page no. |
|-----------|---|----------|
| 4.1 | Crystal data and refinement details for donor species L ₁ and L ₂ . | 128 |
| 4.2 | Crystal data and refinement details for complexes C ₁ , C _{2a} and C _{2b} . | 129 |
| 4.3 | Crystal data and refinement details for complexes C ₃ , C ₄ and C ₅ . | 130 |
| 4.4 | Selected bond lengths (Å) and bond angles (°) for C ₁ . | 131 |
| 4.5 | Selected bond lengths (Å) and bond angles (°) for C _{2a} . | 132 |
| 4.6 | Selected bond lengths (Å) and bond angles (°) for C _{2b} . | 133 |
| 4.7 | Selected bond lengths (Å) and bond angles (°) for C ₃ . | 134 |
| 4.8 | Selected bond lengths (Å) and bond angles (°) for C ₄ . | 135 |
| 4.9 | Selected bond lengths (Å) and bond angles (°) for C ₅ . | 136 |

Chapter V

| Table no. | Title of the table | Page no. |
|-----------|---|----------|
| 5.1 | Crystal data and refinement details for complex C ₁ and uranyl nitrate. | 169 |

| | | |
|-----|--|-----|
| 5.2 | Selected bond lengths (Å) and bond angles (°) for C₁ . | 170 |
|-----|--|-----|

Chapter VI

| Table no. | Title of the table | Page no. |
|-----------|---|----------|
| 6.1 | Crystal data and refinement details for complexes C₁ and C₂ . | 199 |
| 6.2 | Selected bond lengths (Å) and bond angles (°) for C₁ . | 200 |
| 6.3 | Selected bond lengths (Å) and bond angles (°) for C₂ . | 201 |

Abbreviations used

| | |
|------------------|--------------------------------|
| THF | Tetrahydrofuran |
| TFA | Trifluoroacetic acid |
| <i>N,N'</i> -DMF | <i>N,N'</i> -Dimethylformamide |
| DMSO | Dimethyl sulfoxide |
| IR | Infrared |
| Hz | Hertz |
| MHz | Mega Hertz |
| h | Hour |
| g | Gram |
| M | Molar |
| m.p. | Melting point |
| equiv. | Equivalent |
| mmol | Millimole |
| Anal. Calcd. | Analytically calculated |
| NMR | Nuclear magnetic resonance |
| mL | Milliliter |
| s | singlet |
| d | doublet |
| dd | double doublet |
| t | triplet |
| m | multiplet |
| br | broad |
| ppm | parts per million |