STUDIES ON REACTIVITY AND STRUCTURAL ASPECT OF URANYL(VI) ION WITH O, N AND S/Se HETEROATOM SUBSTIUTED ORGANIC DERIVATIVES

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DEPARTMENT OF CHEMISTRY
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DECEMBER-2022

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by

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Submitted

In fulfilment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

to the

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI

DECEMBER-2022

Dedicated to

All that I am, or hope to be, I owe to

my beloved grandparents

Smt. Dhaneshwari, Shri. Triveni and Shri. Banwari Yadav

(Heavenly abode)

CERTIFICATE

This is to certify that the thesis entitled, **“Studies on reactivity and structural aspect of uranyl(VI) ion with O, N and S/Se heteroatom substituted organic derivatives”** *being submitted by* ***Mr. Kaushal Kishor Yadav****, 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 him. Mr. Kaushal Kishor Yadav 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.*

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ACKNOWLEDGEMENTS

Firstly, I would like to express my sincere gratitude to my thesis supervisor, ***Prof. Jai Deo Singh,*** *for his continuing support throughout my PhD studies and associated research, as well as his patience, motivation, and vast expertise. His advice was invaluable during research and writing of this thesis. I could not have imagined having a better advisor and mentor for my PhD studies. The completion of my PhD projects would not have been possible without his active involvement during all stages from the conception to the actual culmination of this thesis.*

In addition, sincere thanks to the former and present Head of Chemistry Department, for providing the necessary facilities in the department and keeping them in good working condition.

The staff of the Instrumentation Laboratory of the Chemistry Department also deserves a special mention. I sincerely acknowledge the Council of Scientific and Industrial Research (CSIR), *Government of India for providing the financial assistance to carry out my research work. My sincere thanks to Prof. R. J. Butcher, Dept. of Chemistry, Howard University, Washington D.C., USA for generously helping me in solving the single crystal data.*

Lab mates play a vital role during the research work of a student. I would like to thank Dr. Abhishek Kumar, Dr. Shipra Yadav, Dr. Jagriti Singh, Deepa Bhardwaj, Jyoti, Preeti Mishra, Dharmendra, and Rahul. I also wish to express my appreciation and warm feelings to my colleagues, Jyoti, and Deepa for giving me a healthy and friendly support in the laboratory.

Heartiest thanks to all my friends whom I met during my stay in IIT Delhi. I am very thankful to Priya, Jyotish, Himanshu, Sharan, Govind, Jaydeep, LahurMani, Saytaprakash, *Ashutosh, Ajeet, Avinash, Dhanjay, Ashish and Akhilesh for their company in and outside the campus.*

Acknowledgements would be incomplete without giving thanks to my family; this thesis would have been impossible without their support. My heartiest thanks to my mother **Mrs. Vimla Devi** *and father* **Mr. Chet Narayan Yadav** *for raising me to believe that anything was possible. I would like to thank my siblings, Mrs. Geeta, Mrs. Sarika, Ms. Babita, Mr. Nand Kishor and Mr. Raj Kishor Yadav for their unfailing love and support.*

Last but not the least I would like to mention a note of love to the kids of my family, Anshal, Anukriti, Aradhya, and Akshat. Even though we were separated by hundreds of miles, your mesmerising little smiles, made the difficult days bearable.

Due acknowledgements are to them, whose name are unintentionally missed out despite their help for this thesis.

Kaushal Kishor Yadav

ABSTRACT

The thesis entitled **"Studies on reactivity and structural aspect of uranyl(VI) ion with N, O and S/Se heteroatom substituted organic derivatives"** deals with the study on UO_2^{2+} ion towards a series of acyclic donor species bearing phenolic (–OH), azomethine (–HC=N–), carbonyl (–C=O) and carboxamide (–NH–C=O) based organic functionalities having (O, N and S/Se) donor atoms, which should have been synthesized for assessing the functional activity of uranyl ion in both aqueous and non–aqueous media. The thesis work is organized into six chapters including a general introduction about uranyl chemistry followed by materials and methods and remaining four chapters (III–VI) that explain the current research findings.

Chapter I provides a brief key introduction to the goals and objectives of the current study as well as inorganic chemists view about the behavior of the uranyl (VI) ion in a variety of contexts including coordination chemistry.

Chapter II provides a list of the chemicals and reagents purchased from various sources, together with information on the synthetic processes used to prepare starting materials which are not commercially available. Furthermore, it describes the physicochemical, spectroscopic, and crystallographic methods employed for the characterization of newly synthesized derivatives.

Chapter III provides the synthesis, characterization, and responsive behavior of di– and tripodal carboxamide (O, N hereto atom type donor species) towards UO_2^{2+} in non–aqueous medium. The structural investigation on the interactive behavior of UO_2^{2+} ion and donor species leads to isolation of uranyl complexes formed as a result of hydrolytic activity. Nevertheless, it was observed that carboxamide species with uranyl ion, like other metal ions, have shown hydrolysis nearly at neutral pH in methanol or acetonitrile.

Chapter IV provides the development of donor molecules containing pyridine–2,6–carboxamido functionality. The understanding of UO_2^{2+} ion with these donor functionalities may be rewarding with several interesting findings that may be prove a reasonable experimental tool in understanding the behavior of UO_2^{2+} ion in biological systems. These donor species appeared to have potential for speciation of uranyl ion in both aqueous and non–aqueous media. The isolation of UO_2^{2+} species as $[UO_2(NO_3)_4]^{2-}$ and nonanuclear uranyl complex species well indicated that the carboxamide functionality in current donor systems are reasonably stable and not hydrolysable.

Chapter V provides the binding abilities of 2,6–organoheteroatom disubstituted pyridine–based donor species bearing diamides (–NH–CO–pyridine–CO–NH–) or sulfur (–S–CO–pyridine–CO–S–) incorporated donor functionalities. In natural environment, the mobility of UO_2^{2+} ion is much influenced with the presence of H_2O. The reaction outcome suggests that the UO_2^{2+} ion and their interaction with humic substances (being considered and proposed as remedial substrate for nuclear waste disposal) may be not so straightforward with amide functionalities present in humic substances.

Chapter VI provides the synthesis of a sequel of new acyclic Schiff base type organic species bearing donor combinations of phenolic (–OH), carboxylic (COOH), azomethine (–HC=N–) and E (E= S or Se) donor functionalities as coordinating sites to examine their potential in understanding the behavior of UO_2^{2+} ion in non–aqueous medium. The donor species may allow one in exploring supramolecular interest of uranyl chemistry as such possibility are also of great interest in alteration process of spent nuclear fuel in uranyl chemistry.

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, –टेट्रामाइंस, 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 लिगैंड 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 चर (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।

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Abbreviations used

THF	Tetrahydrofuran
TFA	Trifluoroacetic acid
HBr	Hydrobromic acid
DMF	Dimethylformamide
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