

**RESPONSIVE NATURE AND FUNCTIONAL
ACTIVITIES OF $\text{UO}_2(\text{VI})$ ION ON INTERACTION
WITH (O, N) AND (O, N, S/Se) BASED ACYCLIC
AND CYCLIC DONOR BASES**

DEEPA BHARDWAJ



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

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WITH (O, N) AND (O, N, S/Se) BASED ACYCLIC
AND CYCLIC DONOR BASES**

by

DEEPA BHARDWAJ

Submitted

In fulfilment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

to the



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

Dedicated to

All that I am, or hope to be,

I owe to my angelic parents

Mrs. Sushila and Mr. Anil Kumar

and

In memory of my beloved

grandfather Shri Anand Swaroop

(Heavenly abode)

CERTIFICATE

*This is to certify that the thesis entitled, “**Responsive Nature and Functional Activities of UO₂(VI) Ion on Interaction with (O, N) and (O, N, S/Se) Based Acyclic and Cyclic Donor Bases**” being submitted by **Ms. Deepa Bhardwaj**, 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. Deepa Bhardwaj 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:

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विद्या नाम नरस्य कीर्तिर्तुला भाग्यक्षये चाश्रयो
धेनुः कामदुधा रतिश्च विरहे नेत्रं तृतीयं च सा ।।
सत्कारायतनं कुलस्य महिमा रत्नैर्विना भूषणम्
तस्मादन्यमुपेक्ष्य सर्वविषयं विद्याधिकारं कुरु ॥

Sincerely,

Deepa Bhardwaj

ABSTRACT

The thesis entitled “***Responsive Nature and Functional Activities of $\text{UO}_2(\text{VI})$ Ion on Interaction with (O, N) and (O, N, S/Se) Based Acyclic and Cyclic Donor Bases***” deals with the study on UO_2^{2+} ion towards a series of acyclic and cyclic species bearing phenolic ($-\text{OH}$), ($-\text{HC}=\text{N}-$), ($-\text{NH}-$) or ($-\text{S}/\text{Se}-$) groups as donor functionalities for evaluating its functional activity. 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 refers critical introduction on uranyl (VI) ion chemistry as inorganic chemist viewed its behavior in various environments including coordination chemistry, along with the aims and objectives of carrying out the present research work.

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 describes the functional activity of UO_2^{2+} ion in response to acyclic donor species bearing ($-\text{OH}$), ($-\text{HC}=\text{N}-$) and ($-\text{S}/\text{Se}-$) functionalities. The complexes isolated herein were found to be stable in nature with interaction of the anion part to the uranyl moiety. Coordinatively, the behavior of UO_2^{2+} ion with donor species used herein follow the classical pathways of coordination chemistry. The experimental observation of $[\text{UO}_2(\text{OCOCH}_3)_3]^-$ is exceptional as this species has been hypothetically studied to a longer extent for its application in nuclear fuel cycle.

Chapter IV refers to the synthesis, characterization, and behavior of a series of

acyclic and cyclic organic species bearing (O– and N–) donor heteroatoms for their response in the presence of UO_2^{2+} ion. The capturing of uranyl ion by these organic donor species in solution state was noticeable and addressed for their potential as extractants.

Chapter V refers to the responsive behavior of UO_2^{2+} ion towards a series of cyclic species bearing phenolic (–OH), (–HC=N–) or its reduced form (–CH₂NH–) and E (E = S or Se) heteroatom as donor functionalities. The UO_2^{2+} ion with the cyclic species revealed unique behavior of $[\text{NO}_3]^-$ ion in bonding pattern. The different bonding of the $[\text{NO}_3]^-$ ion is of practical significance in actinyl extraction chemistry.

Chapter VI refers to the influential chemistry of UO_2^{2+} ion in cyclic coordination environments of donor species bearing phenolic (–OH), (–HC=N–) (–CH₂NH–) or (–HC=O–) as heteroatoms in a series of acyclic or cyclic geometrical architectures. The outcome and recognition of $[\text{UO}_2(\text{NO}_3)_3]^-$ experimentally in conjunction of cyclic organic species appeared to be the first example to observe unusual bonding of one of the $[\text{NO}_3]^-$ ion within the isolated species $[\text{UO}_2(\text{NO}_3)_3]^-$ as mobile ion. Understanding these bonding differences is important for actinide separations in extraction processes.

शोध प्रबंध का सार

“(ओ, एन) और (ओ, एन, एस / एसई) आधारित अचक्रीय और चक्रीय दाता आधारों के साथ परस्पर क्रिया पर यूरेनिल (VI) आयन की उत्तरदायी प्रकृति और कार्यात्मक गतिविधियाँ” शीर्षक वाली थीसिस, फेनोलिक ($-\text{OH}$), ($-\text{HC}=\text{N}-$), ($-\text{NH}-$) या ($-\text{S}/\text{Se}-$) समूहों को अपनी कार्यात्मक गतिविधि के मूल्यांकन के लिए दाता कार्यात्मकता के रूप में असर करने वाली अचक्रीय और चक्रीय प्रजातियों का यूरेनिल आयन की कार्यात्मक गतिविधि का मूल्यांकन करने के अध्ययन से संबंधित है। थीसिस को यूरेनिल आयन पर परिचय, सामग्री और विधियों पर सामान्य परिचय सहित छह अध्यायों में विभाजित किया गया है और शोध के निष्कर्षों पर चार अध्यायों (III–VI) में चर्चा की गई है। अध्याय I यूरेनिल (VI) आयन रसायन पर महत्वपूर्ण परिचय को संदर्भित करता है क्योंकि अकार्बनिक रसायनज्ञों ने वर्तमान शोध कार्य को अंजाम देने के उद्देश्यों और उद्देश्यों के साथ-साथ समन्वय रसायन विज्ञान सहित विभिन्न वातावरणों में इसके व्यवहार का पता लगाया। 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 सिंथेटिक 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 अचक्रीय दाता प्रजाति असर ($-\text{OH}$), ($-\text{HC}=\text{N}-$) और ($-\text{S}/\text{Se}-$) दाता कार्यात्मकताओं की प्रतिक्रिया में यूरेनिल आयन की कार्यात्मक गतिविधि को संदर्भित करता है। यहां पृथक किए गए परिसरों को प्रकृति में स्थिर पाया गया है, जिसमें यूरेनिल की मात्रा से अक्षुण्ण आयन भाग जुड़े हुए हैं। समन्वित रूप से, यहाँ प्रयुक्त दाता प्रजातियों के साथ यूरेनिल आयन का व्यवहार समन्वय रसायन विज्ञान के शास्त्रीय मार्गों का अनुसरण करता है। इस अध्याय में स्थापित $[\text{UO}_2(\text{OCOCH}_3)_3]^-$ का प्रायोगिक अवलोकन असाधारण है क्योंकि इस प्रजाति का परमाणु ईंधन चक्र में इसके अनुप्रयोग के लिए काल्पनिक रूप से लंबे समय तक अध्ययन किया गया है।

अध्याय IV, यूरेनिल आयन की प्रतिक्रिया के लिए अचक्रीय और चक्रीय कार्बनिक प्रजातियों ($\text{O}-$ और $\text{N}-$) विषम परमाणु दाता की एक श्रृंखला की उपस्थिति में संश्लेषण, लक्षण वर्णन और व्यवहार को संदर्भित करता है। समाधान अवस्था में इन कार्बनिक दाता प्रजातियों द्वारा यूरेनिल आयन की पकड़ ध्यान देने योग्य है और निकालने वाले के रूप में उनकी क्षमता के लिए संबोधित किया गया।

अध्याय V, फेनोलिक ($-\text{OH}$), ($-\text{HC}=\text{N}-$) या इसके कम रूप ($-\text{CH}_2\text{NH}-$) और E ($\text{E} = \text{S}$ या Se) विषम परमाणु दाता कार्यक्षमता के रूप में असर करने वाली चक्रीय प्रजातियों की एक श्रृंखला के प्रति यूरेनिल आयन के प्रतिक्रियाशील व्यवहार को संदर्भित करता है। इस अध्याय में स्थापित चक्रीय प्रजातियों के साथ यूरेनिल आयन ने बंधन तरीकों में $[\text{NO}_3]^-$ आयन के अद्वितीय व्यवहार का खुलासा किया। $[\text{NO}_3]^-$ आयन के बारे में अलग-अलग तरीके से संबंधित जानकारी एक्टिनाइड निष्कर्षण रसायन विज्ञान में व्यावहारिक महत्व की है।

अध्याय VI, फेनोलिक ($-\text{OH}$), ($-\text{HC}=\text{N}-$) ($-\text{CH}_2\text{NH}-$) या ($-\text{HC}=\text{O}-$) दाता प्रजातियों के चक्रीय समन्वय वातावरण में यूरेनिल आयन के प्रभावशाली रसायन शास्त्र को चक्रीय की एक श्रृंखला में विषम परमाणु के रूप में संदर्भित करता है। $[\text{UO}_2(\text{NO}_3)_3]^-$ का प्रयोगात्मक रूप से चक्रीय कार्बनिक प्रजातियों के संयोजन के परिणाम और मान्यता पृथक प्रजातियों के भीतर $[\text{NO}_3]^-$ आयन में से एक के $[\text{UO}_2(\text{NO}_3)_3]^-$ मोबाइल आयन के रूप में असामान्य बंधन का निरीक्षण करने के लिए पहला उदाहरण प्रतीत होता है। निष्कर्षण प्रक्रियाओं में एक्टिनाइड पृथक्करण के लिए इन संबंध अंतरों को समझना महत्वपूर्ण है।

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Abbreviations used

THF	Tetrahydrofuran
TFA	Trifluoroacetic acid
HBr	Hydrobromic acid
DMF	Dimethylformamide
IR	Infrared
Hz	Hertz
MHz	Mega Hertz
hr	Hour
g	Gram
M	Molar
m.p.	Melting point
equiv.	Equivalent
mmol	Millimole
Anal. Calcd.	Analysis calculated
NMR	Nuclear magnetic resonance
mL	Millilitre
s	singlet
d	doublet
dd	double doublet
t	triplet
m	multiplet
br	broad
ppm	parts per million
IL	ionic liquid