

**FUNCTIONAL ACTIVITY OF URANYL (UO_2^{2+}) ION IN
RESPONSE TO BIOLOGICALLY RELEVANT
HETEROATOMIC ORGANIC DONOR SUBSTRATES**

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INDIAN INSTITUTE OF TECHNOLOGY DELHI
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RESPONSE TO BIOLOGICALLY RELEVANT
HETEROATOMIC ORGANIC DONOR SUBSTRATES**

by

**PREETI MISHRA
DEPARTMENT OF CHEMISTRY**

Submitted

In fulfilment of the requirements of the degree of Doctor of Philosophy

to the



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This thesis is dedicated to my parents.

For their endless love, support, and encouragement

CERTIFICATE

*This is to certify that the thesis entitled, “**Functional Activity of Uranyl (UO_2^{2+}) Ion in Response to Biologically Relevant Heteroatomic Organic Donor Substrates**” being submitted by **Ms. Preeti Mishra**, 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. Preeti Mishra 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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Preeti Mishra

ABSTRACT

The thesis entitled “*Functional Activity of Uranyl (UO_2^{2+}) Ion in Response to Biologically Relevant Heteroatomic Organic Donor Substrates*” deals with the study on functional activity of UO_2^{2+} ion towards a series of acyclic species bearing phenolic ($-\text{OH}$), ($-\text{HC}=\text{N}-$), ($-\text{C}=\text{O}$) and ($-\text{NH}-\text{N}-$) organic donor functionalities in non-aqueous medium. The thesis is divided into six chapters including concise introduction on chemistry of uranyl ion in view of current study and further their potential application in nuclear technology, post consequences and environmental impact and remediation followed by chapter II as, materials and methods, and findings of the current research work are discussed in four chapters (III–VI).

Chapter I provides a key introductory note envisioned by inorganic chemist and further their contribution towards the study on the behavior of uranyl (VI) ion in diverse environments. The current work is one of the academic, curiosity-driven research in uranyl chemistry and have their potential in advancement of safer use of nuclear technology.

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

Chapter III discusses interactive behavior of UO_2^{2+} with N_4O_3 -type organic species having ‘O’ (oxygen) of phenolic ($-\text{OH}$), ‘N’ of azomethine ($-\text{HC}=\text{N}-$) and imidazolidine donor functionalities derived from the reaction of triethylenetetramine and hydroxy aromatic aldehydes. The behavior of donor species was specific for UO_2^{2+} ion as donor species act as tripodal donor and have tendency to encapsulate uranyl ion in its oxidation state (VI). It was believed that they may act as suitable donor species for UO_2^{2+}

sensing but at the same time the steric constraints imposed by donor species on uranyl ion appeared to be paramount. The critical behavior of H₂O during crystallization in MeOH or CH₃CN as solvent resulted unexpected uranyl ion speciation.

Chapter IV discusses the complexation studies of UO₂²⁺ with symmetrically substituted guanidine-based donor species (with ‘O’ and ‘N’ donor functionalities) derived from the reaction of hydroxy aromatic aldehydes and triaminoguanidine chloride. In addition to the usual coordination ability of donor species, they may also act as an interesting building block in making UO₂²⁺ based supramolecular structures. The hydrolysis reaction followed by carboxamide bond formation may have its worth in studying decorporation of UO₂²⁺ ion in biological system.

Chapter V discusses to study the complexation reactions of UO₂²⁺ with organic species derived from isophthalohydrazide and benzene 1,3,5-tricarbohydrazide and aromatic aldehydes. The donor species may exhibit keto-enol, keto-enamine, *E/Z* isomerization and [–C=N–N=C(O)] tautomerization under reaction conditions. Therefore, an understanding of external influences such as solvent, pH changes, light, heat etc. may further play crucial role in explaining the chemistry of uranyl ion in natural environment.

Chapter VI discusses the complexation reactions of UO₂²⁺ with donor species, bearing ‘O’ of phenolic (–OH), ‘O’ of carboxamide (C=O), ‘N’ of azomethine (–HC=N–) and ‘N’ of pyridine donor functionalities derived from pyridine-2,6-dicarbohydrazide. The interaction of UO₂²⁺ with these donor species resulted trinuclear, tetranuclear and hexanuclear uranyl complexes. Herein, the formation of uranyl complexes of higher nuclearity were found beyond classical explanation of their coordination chemistry. The unprecedented formation of peroxo- and carbonato bridged uranyl complexes were main achievement of this chapter. Peroxo linkage formation may be supported by intrusion of O₂ or formation of –O–O– bond by photolytic manner.

शोध प्रबंध का सार

"जैविक रूप से प्रासंगिक हेटेरोएटोमिक ऑर्गेनिक डोनर सबस्ट्रेट्स के जवाब में यूरेनिल (UO_2^{2+}) आयन की कार्यात्मक गतिविधि" शीर्षक वाली थीसिस, फेनोलिक ($-\text{OH}$), ($-\text{HC}=\text{N}$) वाले चक्रीय प्रजातियों की एक श्रृंखला की ओर UO_2^{2+} आयन की कार्यात्मक गतिविधि पर अध्ययन से संबंधित है। ($-\text{C}=\text{O}$) और ($-\text{NH}-\text{N}-$) गैर-जलीय माध्यम में कार्बनिक दाता कार्यात्मकताएं। थीसिस को छह अध्यायों में विभाजित किया गया है, जिसमें वर्तमान अध्ययन के मद्देनजर यूरेनिल आयन के रसायन विज्ञान पर संक्षिप्त परिचय और परमाणु प्रौद्योगिकी में उनके संभावित अनुप्रयोग, पोस्ट परिणाम और पर्यावरणीय प्रभाव और उपचार के बाद अध्याय II के रूप में, सामग्री और विधियाँ, और निष्कर्ष शामिल हैं। वर्तमान शोध कार्य पर चार अध्यायों (III-VI) में चर्चा की गई है।

अध्याय I अकार्बनिक रसायनज्ञ द्वारा परिकल्पित एक महत्वपूर्ण परिचयात्मक नोट प्रदान करता है और विविध वातावरणों में यूरेनिल (VI) आयन के व्यवहार पर अध्ययन के लिए उनके योगदान को आगे बढ़ाता है। वर्तमान कार्य यूरेनिल रसायन विज्ञान में अकादमिक, जिज्ञासा-संचालित अनुसंधानों में से एक है और परमाणु प्रौद्योगिकी के सुरक्षित उपयोग की उन्नति में उनकी क्षमता है।

अध्याय II विभिन्न स्रोतों के माध्यम से खरीदे गए रसायनों और अभिकर्मकों की सूची प्रदान करता है और प्रारंभिक सामग्रियों की तैयारी के लिए अपनाई जाने वाली सिंथेटिक प्रक्रियाओं का विवरण जो व्यावसायिक रूप से उपलब्ध नहीं थे। 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 में N_4O_3 -प्रकार की जैविक प्रजातियों के साथ UO_2^{2+} के पारस्परिक व्यवहार पर चर्चा की गई है, जिसमें फेनोलिक ($-\text{OH}$) की 'O' (ऑक्सीजन), एज़ोमेथीन की 'N' ($-\text{HC}=\text{N}-$) और इमिडाज़ोलिडिन डोनर कार्यात्मकताएँ हैं, जो ट्राइएथाइलनेटेट्रामिन और की प्रतिक्रिया से प्राप्त होती हैं। हाइड्रॉक्सी एरोमैटिक एल्डिहाइड। डोनर प्रजाति का व्यवहार UO_2^{2+} आयन के लिए विशिष्ट था क्योंकि डोनर प्रजाति ट्राइपोडल डोनर के रूप में कार्य करती है और इसकी ऑक्सीकरण अवस्था (VI) में यूरेनिल आयन को एनकैप्सुलेट करने की प्रवृत्ति होती है। यह माना जाता था कि वे UO_2^{2+} संवेदन के लिए उपयुक्त दाता प्रजातियों के रूप में कार्य कर सकते हैं, लेकिन साथ ही यूरेनिल आयन पर दाता प्रजातियों द्वारा लगाए गए स्टेरिक अवरोध सर्वोपरि प्रतीत होते हैं। MeOH या CH_3CN में विलायक के रूप में क्रिस्टलीकरण के दौरान H_2O के महत्वपूर्ण व्यवहार के परिणामस्वरूप अप्रत्याशित यूरेनिल आयन जाति का उद्भव हुआ।

अध्याय IV हाइड्रॉक्सी एरोमैटिक एल्लिहाइड और ट्रायमिनोगुआनिडाइन क्लोराइड की प्रतिक्रिया से प्राप्त सममित रूप से प्रतिस्थापित गुआनिडीन-आधारित दाता प्रजातियों ('O' और 'N' दाता कार्यात्मकताओं के साथ) के साथ UO_2^{2+} के जटिल अध्ययन पर चर्चा करता है। दाता प्रजातियों की सामान्य समन्वय क्षमता के अलावा, वे UO_2^{2+} आधारित सुपरमॉलेक्यूलर संरचनाओं को बनाने में एक दिलचस्प बिल्डिंग ब्लॉक के रूप में भी कार्य कर सकते हैं। जैविक प्रणाली में UO_2^{2+} आयन की सजावट का अध्ययन करने के लिए कार्बोक्सामाइड बांड गठन के बाद होने वाली हाइड्रोलिसिस प्रतिक्रिया इसके लायक हो सकती है।

अध्याय V में आइसोप्यालोहाइड्राज़ाइड और बेंजीन 1,3,5-ट्राईकार्बोहाइड्राज़ाइड और सुगंधित एल्लिहाइड से प्राप्त कार्बनिक प्रजातियों के साथ UO_2^{2+} की जटिल प्रतिक्रियाओं का अध्ययन करने के लिए चर्चा की गई है। दाता प्रजातियां प्रतिक्रिया स्थितियों के तहत केटो-एनोल, केटो-एनामाइन, *E/Z* आइसोमेराइजेशन और $[-C=N-N=C(O)]$ टॉटोमेराइजेशन प्रदर्शित कर सकती हैं। इसलिए, बाहरी प्रभावों जैसे कि विलायक, pH परिवर्तन, प्रकाश, गर्मी आदि की समझ आगे चलकर प्राकृतिक वातावरण में यूरेनिल आयन के रसायन को समझने में महत्वपूर्ण भूमिका निभा सकती है।

अध्याय VI दाता प्रजातियों के साथ UO_2^{2+} की जटिल प्रतिक्रियाओं पर चर्चा करता है, जिसमें फेनोलिक ($-OH$) का 'O', कार्बोक्सामाइड का 'O' ($C=O$), एज़ोमेथिन का 'N' ($-HC=N-$) और 'N' होता है। पिरिडीन-2,6-डाइकार्बोहाइड्राज़ाइड से प्राप्त पिरिडीन डोनर फ़ंक्शंस। इन दाता प्रजातियों के साथ UO_2^{2+} की अन्योन्य क्रिया के परिणामस्वरूप ट्रिन्यूक्लियर, टेट्रान्यूक्लियर और हेक्सान्यूक्लियर यूरेनिल कॉम्प्लेक्स होते हैं। इसमें, उनके समन्वय रसायन विज्ञान के शास्त्रीय स्पष्टीकरण से परे उच्च परमाणुता के यूरेनिल परिसरों का निर्माण पाया गया। इस अध्याय की मुख्य उपलब्धि पेरोक्सो- और कार्बोनेटो ब्रिज्ड यूरेनिल कॉम्प्लेक्स का अभूतपूर्व गठन था। पेरोक्सो लिंकेज गठन O_2 के घुसपैठ या फोटोलिटिक तरीके से $-O-O-$ बॉन्ड के गठन द्वारा समर्थित हो सकता है।

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LIST OF ABBREVIATIONS

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

LIST OF TABLES

CHAPTER 1

Table 1.1: Projected table is based on reported physical properties available on actinides (Ac-Lr) in various standard textbooks) (For e.g., Cotton, F.A.; Wilkinson, G.; Murillo, C.A.;Bochmann, M. Advanced inorganic chemistry, 6th Edition, Wiley and Sons, New York, 1999).....	6
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