

STUDIES ON URANYL (UO_2^{2+}) ION ACTIVITY WITH (N, O) BASED ACYCLIC ORGANIC DONOR SPECIES

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MAY 2026**

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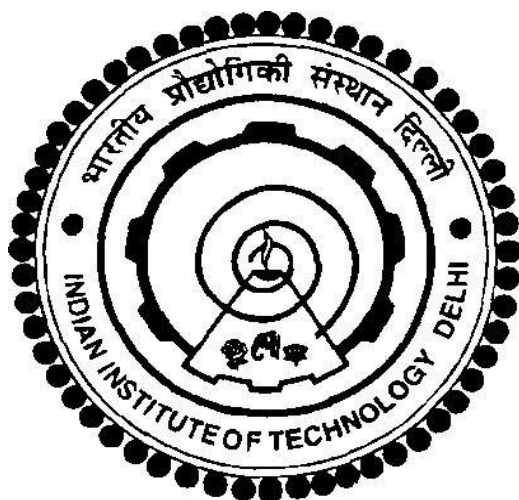
**Studies on Uranyl (UO_2^{2+}) Ion Activity with (N, O) based Acyclic
Organic Donor Species**

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Submitted

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



Chemistry Department

INDIAN INSTITUTE OF TECHNOLOGY DELHI

May 2026

Dedicated to

In Memory of My Grandmother and Grandfather

Smt. Jwala Devi and Sh. Basti Ram Yadav

(Heavenly abode)

And

My beloved parents

Smt. Brham Lata and Sh. Rajender Kumar

My Sister-in-Law and Brother

Mrs. Jyoti Yadav and Mr. Deepender Yadav

Certificate

*This is to certify that the thesis entitled, “**Studies on Uranyl (UO_2^{2+}) Ion Activity with (N, O) based Acyclic Organic Donor Species**”, being submitted by **Mr Rahul Yadav**, 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 him. Mr. Rahul 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 fully to any other University or Institute for award of any degree or diploma.*

Date: 15 May 2026

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ACKNOWLEDGEMENTS

*I would like to thank my research supervisor, **Prof. Jai Deo Singh**, for his guidance, encouragement, and support throughout my research work. You have been a great mentor for me, and your guidance on both research and my career has been invaluable. I could not have imagined having a better mentor for my research work.*

*I am thankful to **Prof. S. Nagendran** (Head), **Prof. Sidharth Pandey**, and **Prof. N.D. Kurur** (former Heads), Department of Chemistry, IIT Delhi, for providing departmental facilities during my research work.*

My sincere thanks also go to Mr Alok, Mr Manoj and Mrs Poornima for helping me in NMR instrumentations, the entire instrumental lab staff, Department of Chemistry, IIT Delhi, for physicochemical and spectral studies throughout the course of research work.

*I would like to express my special thanks to **Prof. Ray J. Butcher**, Dept. of Chemistry, Howard University, Washington D.C., U.S.A., for helping me in determining crystal structures of some of the complexes during the research work.*

I am very thankful to all M.Sc. lab staff, especially Mr Bhupendra Singh, for providing space as well as some common laboratory chemicals to carry out experimental work.

*I sincerely acknowledge the **University Grant Commission (UGC)**, Government of India for providing the financial assistance to carry out my research work.*

I would like to extend my gratitude to all senior members of my research laboratory for their continuous support and suggestions.

I am specially thankful to my friend Dr. Priyanka Chauhan. I am also thankful to my senior Dr. Sanjay Singh and my friends Ravi Saini, Subham, Abhijeet Singh and Dr Aishwariya Chauhan.

My special thanks to my laboratory colleagues, Dharmendra, Raj Sarkar, Bhupinder, Manoj, Deepanderpal, Kapil, Divyansh, Mohit and Priyanka for their healthy and friendly support and encouraging scientific atmosphere in the laboratory.

Words fail to express my sentiments for my loving and respectable parents (Mrs Brham Lata & Mr Rajender Kumar) for raising me to be what I am today, believing in me, giving me freedom and space to grow. I dedicate this work, this thesis, to you both, Mummy and Papa.

I would also like to thank my siblings Deepender, Jyoti, Gulshan, Pinki, Pawan, Sunny, and Sania for their infallible love and support. The list is incomplete without acknowledging my cute little nephew, Preet Yadav, whose small activities always made me smile in challenging periods.

Rahul Yadav

ABSTRACT

The uranyl ion (UO_2^{2+}) is a foundation of actinide chemistry, yet its "hidden" electronic and bonding characteristic remains a major challenge for chemists to precisely ascertain. The hidden and factual chemistry of UO_2^{2+} ion remain under investigations and presents major challenges for chemists to be precisely ascertained. Integrating inorganic, organic, and biological functionalities into a single donor system is a refined way to probe how different chemical environments influence the UO_2^{2+} core. Addressing the challenges associated with uranyl ion (UO_2^{2+}) is critical for managing decades of accumulated, unsafe nuclear waste.

Keeping the established views on uranyl ion chemistry and further to advance the understanding, the current research in the form thesis entitled “*Studies on Uranyl (UO_2^{2+}) Ion Activity with (N,O) Based Acyclic Organic Donor Species*” was undertaken for further exploration. This research aims to advance understanding of how acyclic ligands, specifically those containing both Nitrogen (N) and Oxygen (O) donor interact with the linear uranyl ion in non-aqueous solvent medium.

Chapter 1 provides a concise and critical survey of the peculiar chemistry of UO_2^{2+} ion and its relevance for current study. This also includes significance in understanding behavior of UO_2^{2+} ion in aqueous/non-aqueous medium. This also describe about the uranyl ion chemistry with the objectives of current study in perception of the contribution of an inorganic chemist.

Chapter 2 summarizes the physicochemical techniques, such as elemental analysis (C, H, N), UV-Vis, IR, ESI-MS, and NMR (^1H and ^{13}C) spectroscopic methods used for identification of newly synthesized derivatives. Single-crystal X-ray diffraction studies also have been carried out wherever; suitable crystals were obtained. Successively the findings and results with discussion of present research work have been addressed in the Chapter 2-6.

Chapter 3 details the synthesis of di- and trinuclear uranium (VI) complexes of stationary Schiff bases derived from hydroxyaromatic aldehyde and aminophenol derivatives. The formation of

$[(\text{UO}_2)_3(\mu_3\text{-O})(\text{L}1)_3]^{2-}$ or $[(\text{UO}_2)_3(\mu_3\text{-O})(\text{sap})_3]^{2-}$ (where sap = *N*-salicylidene-2-aminophenolato) as trinuclear oxo-bridged complex via the coordination of a water molecule in deprotonated form. The ($\mu_3\text{-O}$) anion (oxygen atom) bind three donor coordinated uranyl ions in a triangular arrangement where each uranyl (VI) attained pentagonal bipyramidal coordination arrangement. The isolated species also features a central ($\mu_3\text{-O}$) bridge (an oxygen atom shared by three uranyl species) adopts a pentagonal bipyramidal geometry, where the equatorial plane is covered by the donor species and bridging oxo-anion.

Chapter 4 details the Synthesis and structural aspects of uranyl complexes accessible from the donor bases derived from the reaction of *o*-hydroxy aromatic aldehydes and 2-Amino-2-(hydroxymethyl)-1,3-propanediol. The donor species allow the formation of a mononuclear species in solution however, obtained as dinuclear species in crystalline form. Single-crystal X-ray diffraction analysis revealed a dinuclear structure with characteristic pentagonal bipyramidal geometry around the $\text{UO}_2^{2+}(\text{VI})$ centre.

Chapter 5 details the mononuclear uranium (VI) complexes derived from prominent *salophen* and related Schiff *bases* bearing (ONNO) and (ONNNO) donor atoms. Herein, uranyl complexes derived from donor species *N,N'*-bis(salicylaldehyde)-1,2-phenylenediimino (*salophen*), *N,N'*-bis(2-hydroxy-1-naphthaldimine)-*o*-phenylenediamine and bis-(2-hydroxy-1-naphthaldimine)-*N*-diethylenetriamine (*naphthyl-salophen*) with definite access of equatorial ONNO (N_2O_2) and (ONNNO) (N_3O_2) donor planes for linear uranyl ions have been synthesized and characterized. ESI-MS studies has proven significant in speciation of the complexation reaction of donor species and uranyl ions (UO_2^{2+}). It revealed presence of both major and minor species in solution along with the formation of high-nuclearity complexes.

Chapter 6 details the Synthesis of acyclic ($\text{N}_5\text{O}_2/\text{N}_5\text{O}_3$) donor species occasioning as mixture from condensation of tetraethylpentaamine and hydroxyl-aromatic aldehydes and their UO_2^{2+} complexes. The uranyl species crystallized from reaction solution with a donor species bearing robust imidazolidine based (N_5O_3) species compared to the linear chain (N_5O_2) donor species present in

reaction mixture. The formation of uranyl complexes UO_2L_1 and UO_2L_2 from mixture of organic species ($\text{H}_3\text{L}_1/\text{H}_3\text{L}'_1\text{-H}_3\text{L}_3/\text{H}_3\text{L}'_3$) is confirmed by ESI-MS. Under the experimental condition herein, only (1:1) (M:L) complexes were obtained from the reaction mixture present in CH_3CN . These studies also allowed in understanding mechanistic pathways of coordination process via uranium speciation in non-aqueous systems and the ability of separation of a complex species derived from rigid donor systems.

Hence, understanding the trends in chemistry and structural diversity of alteration products of primary (or first formed) uranium compounds is important for predicting long-term behavior of radioactive wastes in geological repositories and their geochemical migration. Since, some of the uranyl species as a consequence of chemical processes provide alteration phases that may incorporate radionuclides into their structures. These compounds, mainly peroxy-uranium species, are often considered as transporting agents both in geological media and in deposits of spent nuclear fuel. Consequently, the study of uranyl compounds is essential for both developing more efficient, sustainable nuclear energy systems and for environmental remediation

शोध प्रबंध का सारांश

यूरानिल आयन (UO_2^{2+}) एक्टिनाइड रसायन शास्त्र की एक नींव है, फिर भी इसकी "छिपी हुई" इलेक्ट्रॉनिक और बांडिंग विशेषताएँ रसायनज्ञों के लिए सटीक रूप से पता लगाना एक बड़ी चुनौती बनी हुई हैं। (UO_2^{2+}) आयन की छिपी और वास्तविक रसायन शास्त्र अभी भी अनुसंधान के अधीन है और इसे सटीक रूप से जानने के लिए रसायनज्ञों के सामने बड़ी चुनौतियाँ प्रस्तुत करता है। अकार्बनिक, कार्बनिक और जैविक कार्यात्मकताओं को एक ही डोनर सिस्टम में एकीकृत करना यह जानने का एक परिष्कृत तरीका है कि विभिन्न रासायनिक वातावरण (UO_2^{2+}) कोर को कैसे प्रभावित करते हैं। यूरानिल आयन (UO_2^{2+}) से संबंधित चुनौतियों का सामना करना दशकों से संचित, असुरक्षित परमाणु अपशिष्ट को प्रबंधित करने के लिए महत्वपूर्ण है।

यूरानिल आयन रसायन विज्ञान पर स्थापित दृष्टिकोण को ध्यान में रखते हुए और आगे की समझ को बढ़ाने के लिए, वर्तमान शोध थीसिस के रूप में यूरानिल (UO_2^{2+}) आयन की गतिविधि का (N,O) आधारित एसाइक्लिक ऑर्गेनिक डोनर प्रजातियों के साथ अध्ययन शीर्षक के तहत आगे की खोज के लिए किया गया। इस शोध का उद्देश्य यह समझना है कि एसाइक्लिक लिगेंड, विशेष रूप से उन में नाइट्रोजन (N) और ऑक्सीजन (O) दोनों डोनर होते हैं, गैर-जलघुलनशील सॉल्वेंट माध्यम में रेखिक यूरानिल आयन के साथ कैसे इंटरैक्ट करते हैं।

अध्याय :1 (UO_2^{2+}) आयन की विशिष्ट रसायन विज्ञान का संक्षिप्त और महत्वपूर्ण सर्वेक्षण प्रस्तुत करता है और वर्तमान अध्ययन के लिए इसकी प्रासंगिकता को दर्शाता है। इसमें ताजगी के साथ (UO_2^{2+}) आयन के जल/गैर-जल माध्यम में व्यवहार को समझने का महत्व भी शामिल है। यह वर्तमान अध्ययन के उद्देश्यों के साथ यूरानिल आयन रसायन विज्ञान का वर्णन करता है, जो एक अकार्बनिक रसायनज्ञ के दृष्टिकोण में योगदान की धारणा को दर्शाता है।

अध्याय: 2 में भौतिक-रासायनिक तकनीकों का सारांश प्रस्तुत किया गया है, जैसे कि तत्वीय विश्लेषण (C, H, N), UV-Vis, IR, ESI-MS, और NMR (^1H और ^{13}C) स्पेक्ट्रोस्कोपिक विधियाँ जो नव-निर्मित व्युत्पन्नों की पहचान के लिए उपयोग की गईं। एकल-संरचना वाले X-रे विकिरण अध्ययन भी किए गए हैं जहाँ भी उपयुक्त क्रिस्टल प्राप्त हुए। इसके बाद वर्तमान शोध कार्य के निष्कर्ष और परिणामों की चर्चा अध्याय 2-6 में प्रस्तुत की गई है।

अध्याय: 3 स्थिर शिफ बेसों के हाइड्रॉक्सीएरोमैटिक एल्डीहाइड और एमिनोफेनोल व्युत्पन्नों से प्राप्त डाय- और ट्राइन्यूक्लियर यूरेनियम (VI) जटिलों के संश्लेषण का विवरण देता है। $[(UO_2)_3(\mu_3-O)(L_1)_3]^{2-}$ या $[(UO_2)_3(\mu_3-O)(sap)_3]^{2-}$ (जहाँ sap = N-सैलिसिलिडीन-2-एमिनोफेनोलाटो) का निर्माण एक ट्राइन्यूक्लियर ऑक्सो-ब्रिज्ड जटिल के रूप में डिप्रोटोनेटेड स्वरूप में पानी अणु के संयोजन के माध्यम से होता है। (μ_3-O) आयन (ऑक्सीजन परमाणु) तिहरे डोनर संयोजित यूरायिल आयनों को त्रिभुजाकार व्यवस्था में बांधता है, जहां प्रत्येक यूरायिल (VI) ने पंचकोणीय द्विपिरामिडीय संयोजन व्यवस्था प्राप्त की। अलग किए गए प्रकार में केंद्रीय (μ_3-O) पुल (एक ऑक्सीजन परमाणु जो तीन यूरायिल प्रजातियों द्वारा साझा किया गया है) भी पंचकोणीय द्विपिरामिडीय ज्यामिति को अपनाता है, जहां समतलीय तल को डोनर प्रजातियों और ब्रिजिंग ऑक्सो-आयन द्वारा कवर किया गया है।

अध्याय: 4 उन यूरानिल कॉम्प्लेक्सों के संश्लेषण और संरचनात्मक पहलुओं का विवरण देता है जो o-हाइड्रॉक्सी एरोमैटिक एल्डिहाइड्स और 2-एमिनो-2-(हाइड्रॉक्सिमैथिल)-1,3-प्रोपेनेडियोल की प्रतिक्रिया से प्राप्त डोनर आधारों से सुलभ हैं। ये डोनर प्रजातियाँ घोल में एक मोनोन्यूक्लियर प्रजाति के निर्माण की अनुमति देती हैं, हालांकि इसे क्रिस्टलीय रूप में डाइन्यूक्लियर प्रजाति के रूप में प्राप्त किया जाता है। सिंगल-क्रिस्टल X-रे विवर्तन विश्लेषण ने UO_2^{2+} केंद्र के चारों ओर विशेष पेंटागोनल बाइपिरामिडल ज्यामिति के साथ डाइन्यूक्लियर संरचना प्रकट की।

अध्याय: 5 प्रमुख सालोफेन और संबंधित शिफ बेस से व्युत्पन्न मोनोन्यूक्लियर यूरेनियम (VI) यौगिकों का विवरण देता है जिनमें (ONNO) और (ONNNO) डोनर एटम होते हैं। यहां, डोनर प्रजातियों N,N'-बिस(सैलिसिलिडिहाइड)-1,2-फेनिलीनडाइमिनो (सालोफेन), N,N'-बिस(2-हाइड्रॉक्सी-1-नेफ्थाल्डाइमिन)-o-फेनिलीनडाइमिन और बिस-(2-हाइड्रॉक्सी-1-नेफ्थाल्डाइमिन)-N-डाइथिलीनट्राइमिन (नेफ्थाइल-सालोफेन) से व्युत्पन्न यूरिल यौगिकों को रेखीय यूरिल आयनों के लिए निश्चित समान्तर ONNO (N_2O_2) और (ONNNO) (N_3O_2) डोनर विमानों के साथ संश्लेषित और वर्णित किया गया है। ESI-MS अध्ययन ने डोनर प्रजातियों और यूरिल आयनों (UO_2^{2+}) के यौगिककरण प्रतिक्रिया की प्रजाति निर्धारण में महत्वपूर्ण साबित किया। इसने समाधान में मुख्य और गौण दोनों प्रजातियों की उपस्थिति को प्रकट किया और उच्च-न्यूक्लियरिटी यौगिकों के निर्माण को भी दिखाया।

अध्याय: 6 में असाइक्लिक (N5O2/ N5O3) डोनर प्रजातियों के संश्लेषण का विवरण दिया गया है, जो टेट्राएथाइलपेंटामाइन और हाइड्रॉक्सी-अरोमैटिक अल्डीहाइड्स के संघनन से मिश्रण के रूप में उत्पन्न होती हैं और उनके UO_2^{2+} कॉम्प्लेक्स। यूरेनिल प्रजातियाँ प्रतिक्रिया द्रावण से क्रिस्टलीकरण करती हैं जिसमें मजबूत इमिडाज़ोलिडिन आधारित (N5O3) प्रजातियों वाला डोनर प्रजाति होती है, जबकि प्रतिक्रिया मिश्रण में मौजूद रैखिक श्रृंखला (N5O2) डोनर प्रजातियाँ होती हैं। ऑर्गेनिक प्रजातियों के मिश्रण ($\text{H3L1/ H3L'1-H3L3/ H3L'3}$) से यूरेनिल कॉम्प्लेक्स UO_2L_1 और UO_2L_2 के निर्माण की पुष्टि ESI-MS द्वारा की जाती है। यहां वर्णित प्रायोगिक परिस्थितियों में, केवल (1:1) (M:L) कॉम्प्लेक्स CH_3CN में मौजूद प्रतिक्रिया मिश्रण से प्राप्त हुए। इन अध्ययनों ने गैर-जलयोज्य प्रणालियों में यूरेनियम प्रजातिकरण के माध्यम से समन्वय प्रक्रिया के यांत्रिक मार्गों को समझने में और कठोर डोनर सिस्टम से उत्पन्न कॉम्प्लेक्स प्रजातियों के पृथक्करण की क्षमता को समझने में योगदान दिया।

इसलिए, प्राथमिक (या पहली बार बने) यूरेनियम यौगिकों के परिवर्तन उत्पादों के रसायन शास्त्र और संरचनात्मक विविधता में रुझानों को समझना भूवैज्ञानिक भंडारों में रेडियोधर्मी अपशिष्टों के दीर्घकालिक व्यवहार और उनके भू-रासायनिक प्रवासन की भविष्यवाणी करने के लिए महत्वपूर्ण है। चूंकि, रासायनिक प्रक्रियाओं के परिणामस्वरूप कुछ यूराइल प्रजातियाँ परिवर्तन चरण प्रदान करती हैं जो अपने ढाँचे में रेडियोन्यूक्लाइड्स को शामिल कर सकती हैं। ये यौगिक, मुख्यतः पेरोक्सी-यूरेनियम प्रजातियाँ, अक्सर भूवैज्ञानिक माध्यमों और खर्च किए गए नाभिकीय ईंधन के निक्षेपों दोनों में परिवहन एजेंट के रूप में मानी जाती हैं। परिणामस्वरूप, यूराइल यौगिकों का अध्ययन अधिक कुशल, स्थायी नाभिकीय ऊर्जा प्रणालियों के विकास और पर्यावरणीय सुधार दोनों के लिए आवश्यक है।

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Abbreviations used

THF	Tetrahydrofuran
TFA	Trifluoroacetic acid
HBr	Hydrobromic acid
DMF	N,N-Dimethylformamide
IR	Infrared
DIPEA	N,N-diisopropylethylamine
Hz	Hertz
MHz	Mega Hertz
h	Hour
g	Gram
M	Molar
mp	Melting point
equiv.	Equivalent
mmol	Milli mole
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