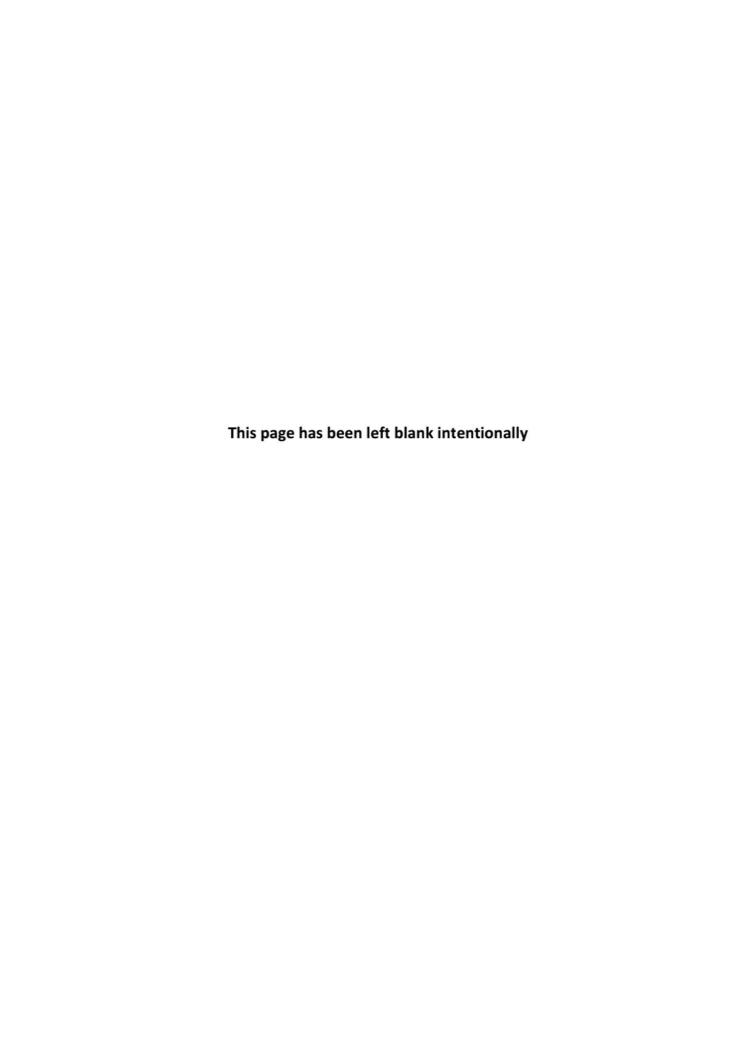


Edited by

Dr. Mahua Dhara (Ganguly)



RECENT ADVANCES IN CHEMISTRY AND CHEMISTRY-BIOLOGY INTERFACE

Editor

Dr. Mahua Dhara (Ganguly)

Department of Chemistry

Vivekananda Satavarshiki Mahavidyalaya



Vivekananda Satavarshiki Mahavidyalaya

Manikpara, Jhargram West Bengal, India PIN – 721513

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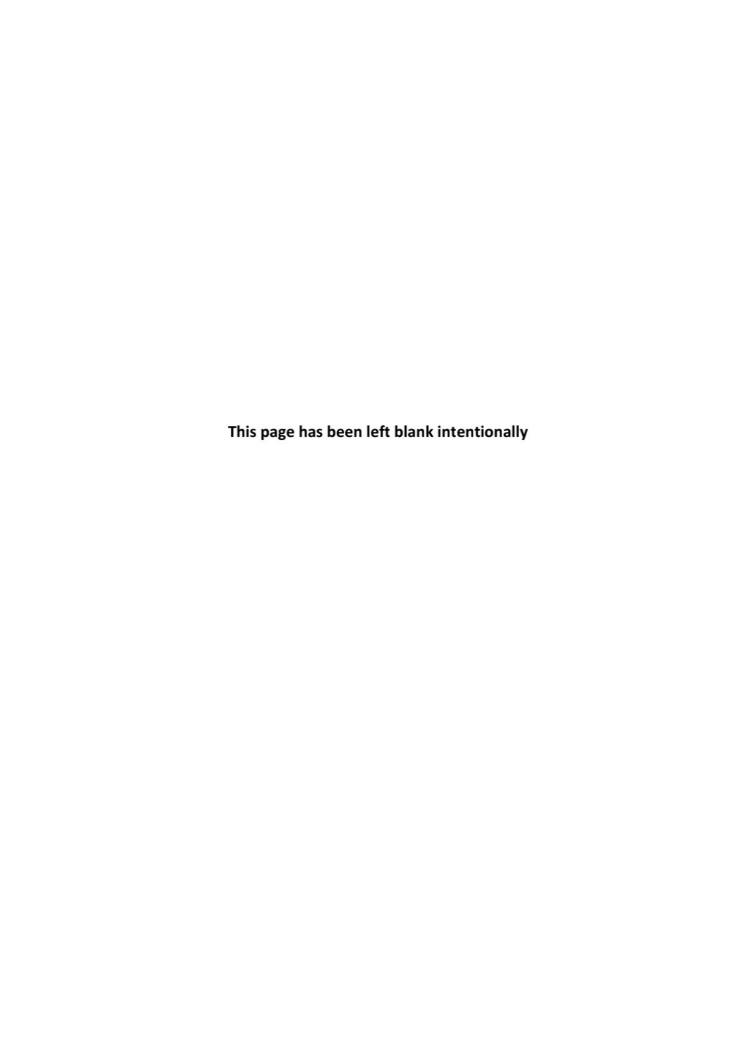
PREFACE

Vivekananda Satavarshiki Mahavidyalaya was established in the year 1964 in commemoration of birth centenary of Swami Vivekananda in a small town called Manikpara, in the district of Jhargram in West Bengal. Starting its journey with a handful of students, teachers and non-teaching staff in a local high school, the college has slowly gained prominence as an institute that offers high quality education, particularly to the less-privileged population in the tribal belt of Jhargram. At present, it has its own sprawling campus accommodating more than 1500 students enrolled in Arts, Science and Commerce streams along with a significantly high number of qualified teaching and non-teaching staff, offering degree courses in thirteen honours and fourteen general subjects. During the last 60 years since its inception, this college has illuminated the minds of thousands of students, especially the women of the nearby villages who have got the opportunity to enrol for higher education and exposure to various job-oriented courses. Being located in a serene place amidst extensive greenery, our college provides the perfect ambience that is conducive for a healthy mind and body.

The Department of Chemistry of this college, with its strong teaching fraternity, has been always striving to reach a level of excellence through quality teaching, publications and hosting international webinars and seminars. There are fourteen chapters in this book that have been authored by teachers of Chemistry of various colleges of West Bengal and are mostly based on research works and review articles presented in a one-day international symposium entitled 'Recent Advances in Chemistry and Chemistry-Biology Interface' organized by the Department of Chemistry of Vivekananda Satavarshiki Mahavidyalaya on 5th January 2024. In the day-long event held within the college premises, a large number of participants, college teachers, research scholars and students got the opportunity to listen and interact with several distinguished scientists and professors from renowned institutes of India and abroad regarding the latest trends in chemistry as well as at the interface of chemistry and biological sciences. All the chapters of this book have been rigorously peerreviewed by professors and scientists of eminent institutes and organizations. The final revised versions of the chapters have been compiled and edited with utmost care and precision so as to make it publishable in its finest form. Hopefully, this book will be of great help to teachers and scientists, particularly the young researchers who are keen to learn new concepts, technologies and explore new horizons while engaging themselves in both teaching and research for career enhancement purposes.

My best wishes to all the readers.

Dr. Mahua Dhara (Ganguly)



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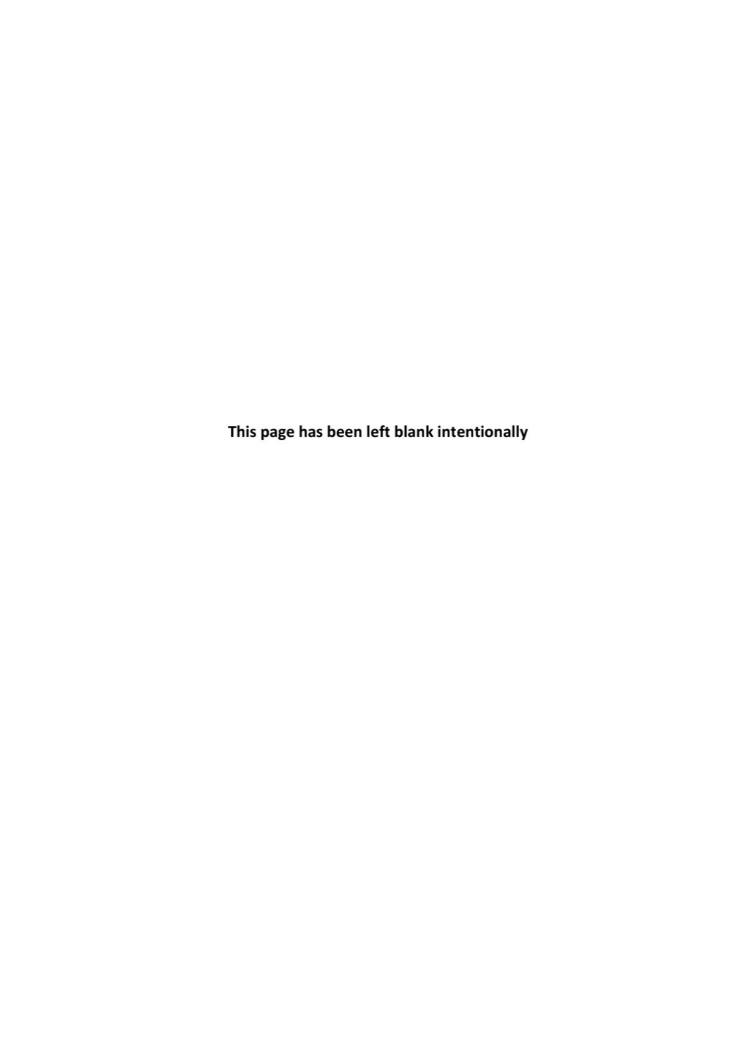
My sincere gratitude to Dr. Souvik Maiti (CSIR-Institute of Genomics and Integrative Biology, New Delhi, India), Dr. Amiya Kumar Panda (Vidyasagar University, West Bengal, India), Dr. Ajay Kumar Misra (Vidyasagar University, West Bengal, India), Dr. Samik Nanda (Indian Institute of Technology Kharagpur, West Bengal, India), Dr. Kausik Mukhopadhyay (University of Central Florida, Orlando, USA), Dr. Rajarshi Samanta (Indian Institute of Technology Kharagpur, West Bengal, India), Dr. Sanjib Kumar Patra (Indian Institute of Technology Kharagpur, West Bengal, India), Dr. Debabrata Dey (Weizmann Institute of Science, Israel) and Dr. Tanaya Bose (CSIR-Indian Institute of Chemical Biology, Kolkata, India) for their valuable contribution towards the success of the symposium.

I am deeply indebted to my fellow colleagues of the Department of Chemistry, Vivekananda Satavarshiki Mahavidyalaya, Professor Tapas Kumar Das, Shri. Surajit Pradhan and Ms. Anwesha Pal for their incredible cooperation and support throughout the journey.

I convey my special thanks to Sri. Subhendu Kar (Librarian) for his valuable inputs regarding editing and publication of this book. My sincere thanks to Dr. Kartik Patra (Department of Mathematics) and Dr. Abdulla Al Mamon (Department of Physics) for there help in organizing the symposium. I am also thankful to Shri Debabrata Acharyya (Office) for his constant support. I am extremely grateful to all the teaching and non-teaching staff of Vivekananda Satavarshiki Mahavidyalaya for their good wishes, warmth and cooperation.

Above all, I thank Almighty God for His blessings without which no endeavour can ever be successful!

Dr. Mahua Dhara (Ganguly)



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DNA Binding and Cleavage Activity of Schiff Base Metal Ion Complexes - A Short Review

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Abstract

Schiff base metal complexes are of great interest due to their diverse application in the field of biological system as well as in molecular magnetism. Design and synthesis of metal based therapeutic drugs draw much attention of the researcher for last few decades. However the interaction between transition metal ion complexes with DNA is the key concept for the investigation of effectiveness of DNA binding anticancer drugs and chemotherapeutic agents. Platinum based drugs was of first choice and cisplatin was the former candidate in this investigation, however the unwanted side effects and health hazards associated with platinum based drugs opened up the door for searching of suitable substitute with improved activity. A number of Schiff base metal ion complexes were tested for their anti-cancerous activity and it was found that cationic character, structural speciality along with other function took the credit for such complexes to bind with DNA and to stop its polymerization and in some cases cleave the DNA. Metal ion complexes of copper, nickel and cobalt are of great interest towards inorganic chemists to focus on clinical applications. From literature it was found that among different transition metal ions Cu(II) is suitable alternative to cisplatin. Cobalt complexes posses antiviral, antimicrobial, antitumor, antioxidant property and found application as anticancer agents. Nickel complexes play vital role in bioinorganic chemistry and they have been examined for inhibition of cancer cell proliferation.

Keywords: Schiff base, DNA binding activity, DNA cleavage activity. Metal ion complex.

1. Introduction

Deoxyribonucleic acid or DNA is a polymeric molecule composed of two polynucleotide chain, coiled around each other to produce a double helix structure. Primary steps involved in cell growth and cell division are DNA replication, transcription and protein synthesis, therefore, the key target for curing cancer is DNA in several anticancer therapies (Sava et al., 2012; Maji & Bhattacharya, 2014). Similarly many antiviral drugs functioning by targeting DNA (Kausar et al., 2021), and terminate their growth.

Research on interactions of DNA with transition metal ion complexes has gained enormous attention due to their wide application in molecular biology and cancer treatment. Interaction between metal complexes with DNA has gained much popularity in recent past due to their variety of applications especially in cancer treatment and molecular biology. Multidentate aromatic ring containing ligands are best candidate in this platform (Parveen S., 2020).

Interaction of such kind of molecule with DNA interfere with different process like DNA replication, transcription etc. Considering this phenomenon different drugs can be designed for the treatment of cancer, cystic fibrosis etc by targeting DNA. Cisplatin is a well-known drug that achieved great clinical success as an anticancerous agent. Cisplatin posses several side effects like nephrotoxicity, ototoxicity, bone marrow suppression, neutrotoxicity, nausea, vomiting etc. (Tchounwou et al., 2021). Therefore, scientist had tried to synthesize different compounds with better potency and reduced side effects and research is still progressing in this area in order for searching of variety of metal ion ligand complexes that result in structural damage to DNA and would be able to restrict the access of necessary proteins to DNA to achieve the basic cellular functions needed for replication and transcription.

2. Schiff base complexes

Schiff base is a significant class of compounds, that can be characterized by formation of imine bonds, by condensation reaction involving primary amine with an active carbonyl group (aldehyde or ketone group). Study of Schiff base ligand has drawn great attention due to their numerous applications in biological field like anticancer (Sumi et al., 2023), anti-inflammatory (Sandhu et al., 2023), antioxidant (Yadav et al., 2021) and also find activity as antitumor (Paul et al., 2021), antimicrobial (Saranya et al., 2020), anti-inflammatory agent (Krishna et al., 2023). Schiff base complexes can coordinate to metal ions by virtue of the donor atoms present in their backbone. Symmetrical Schiff base ligands can stabilize metal ions in various oxidation state. Dinucleating Schiff base ligand can accommodate two metal ions in their coordination pocket. The rigid framework of the ligand helps to stabilize the DNA-schiff base ligand adduct through various kind of interaction. Many Schiff base ligands are reported showing anticancer activity and it has been observed that the activity increases many fold upon inclusion of metal ions (Paul et al., 2021). It has been observed that salicylaldehyde based Schiff base ligands are effective in cleavage of DNA (Mamindla et al., 2023).

3. Transition metal ions

Transition metal ions are the essential bio elements due to their oxidative nature and important enzymatic activity. Among them cobalt, nickel, copper and zinc snatched the limelight due to their clinical application (Molinaro et al., 2020; Wang et al., 2022). Transition metal complexes are important for their nuclease like activity. They have been studied extensively by producing reactive oxygen species, using redox property of the transition metal ions and O₂, which helps the cleavage of DNA either by direct strand scission or by modification of base.

4. DNA binding activity

Interaction between DNA and metal ion complexes are the important field of research and this journey begins with the discovery of cisplatin (Alderden et al., 2006; Ghosh et al., 2019). With the passage of time several new ligand systems have been designed with effective DNA binding activity. In this regards 'NSO' donor Schiff base ligands plays a vital role. Binding of the metal ligand complex with DNA occurs through three modes – groove binding, intercalation and alkylator.

Groove binding does not convince large conformational change in DNA backbone. Two types of groove are present in DNA backbone – major groove (G-C) and minor groove (A-T). Groove binder molecule generally consist of heterocyclic or aromatic moities that fit into either major or minor groove of the double helix with subsequent removal of water.

Intercalation involved insertion of planner molecule between the base pair of DNA, as a result helical twists are decreased and this results to lengthening of DNA. Intercalators are generally planner molecule of aromatic ring or heterocyclic ring. After intercalation the adduct get stability by π - π stacking interaction between ring and DNA base without disrupting the base pairing pattern. This leads to unwinding of DNA double helix by lengthening of the chain upto 3Å per bound drug molecule.

Electrophilic compounds that react with nucleophilic group of DNA forming covalent bond are known as alkylator. The addition of the electrophilic compound leads to inhibition of transcription and translation process (Martinez et al., 2003; Mishina et al., 2006). The N(3) atom of adenine and the N(7) atom of guanine are the most reactive as they are nucleophilic as well as uncovered in the grooves of the DNA duplex (Dong et al., 2021)

5. DNA cleavage activity

DNA cleavage is a vital process in living system in order to protect the cell form foreign substance such as virus by cleavage of foreign DNA or for change in topological state in DNA. Ability of many anticancer drugs depends on the cleavage activity of DNA in affected cell, which trigger apoptosis and finally lead to cell death (Buzun et al., 2020). Three different kind of cleavage activity had been found hydrolytic cleavage, oxidative cleavage and photoinduced DNA cleavage.

Cleavage of phosphodiester bond of DNA to produce fragments in presence of water is known as hydrolytic cleavage of DNA. In general cleavage by water is a very slow process which can be facilitated by presence of metal ion which act as lewis acid. Hydrolysis of DNA occurs by attack of nucleophile to the phosphate backbone. As a result a five coordinated intermediate is formed which then undergoes cleavage with subsequent release of a sugar moiety as alcohol unit.

Oxidative cleavage can takes place either in the ribose sugar moiety or in the nucleobase. The cleavage reaction generally mediated by additive like H₂O₂ or in presence of photoinduced DNA cleaving agent like light. Hydroxy radical species are generally involves in oxidative cleavage process. During oxidative cleavage at deoxyribose sugar abstraction of one H initiate the cleavage process wherever in case of nucleic base oxidation is mostly prefferd at guanine due to its lower oxidation potential.

During photoinduced DNA cleavage light used to trigger cleavage activity. Photosensitized DNA damage can be classified in two category. Type-I is one electron process and type II is the pathway involving singlet oxygen. Type-I process proceed by generation of superoxide radical from molecular oxygen and it act as reductant.

Rodríguez et al. reported the DNA binding and cleavage activity of transition metal ion complexes of an unique heterocyle thiophine containing Schiff base ligand synthesized by condensation reaction between 2-thiophene methyl amine and o-vanillin. Complexes of copper(II), zinc(II) and oxidovanadium(IV) were efficient to interact with DNA but only copper (II) complex was found to have DNA cleavage activity and posses good cytotoxic

activity. It was also observed that only the copper complex bound to the minor groove of DNA owing to its square planner geometry around the copper(II) center, where as zinc(II) and oxidovanadium(IV) complexes with tetrahedral and square pyramidal geometry prefers major groove binding (Rodríguez et al., 2021).

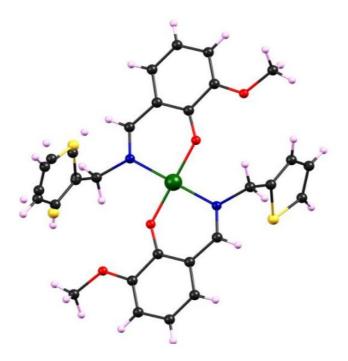


Figure 1. Crystal structure of [Cu(OVATPNH₂)₂]. Colour code: Cu, green; Zn, grey, C, black; O, red; H, pink. (Rodríguez et al., 2021)

Sumi et al. reported a Schiff base ligand CNAT (Figure 2) synthesized by condensation reaction between curcumin and substituted 2-aminothiophene. The ligand was used for synthesis of mononuclear complexes of transition metal ions (Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺) and all the complexes was used to study DNA cleavage activity. It was observed that all the complexes successively cleaved substituted PUC18 plasmid DNA. Mn(II) and Ni(II) complexes completely cleave the DNA and Co(II), Cu(II) and Zn(II) complexes also cleave DNA in a linear form. From molecular docking study binding energy of the cobalt(II) and nickel (II) complexes was found to be -8.21 and -10.04 kcal mol⁻¹ (Sumi et al., 2023).

DNA and cleavage efficiency of 1-(5-(4-fluorophenyl)isoxazol-3binding ylimino)methyl)napthalen-2-ol (L¹) and (2-(5-(4-fluorophenyl)isoxazol-3-ylimino)methyl)-4methylphenol (L²) based metal complexes $[M(L^1)_2]$ and $[M(L^2)_2]$ where M = Co(II), Ni(II), Cu(II)] was investigated (Figure 3) by Ramesh and his coworkers. Binding experiment was carried out using CT-DNA by UV-absorption, fluorescence and viscosity measurement technique and the group reported all the complexes moderately intercalate with CT-DNA. Clevage experiment was performed using PBR3222 plasmid DNA in presence of H₂O₂ (oxidative cleavage) and UV light (photolytic cleavage) with both ligand and metal complexes and it was observed that metal complexes are more efficient in cleavage than ligand. (Ramesh et al., 2020)

Figure 2: Schiff base ligand CNAT (Sumi et al., 2023)

Figure 3: Metal (II) complexes ($M = Cu^{2+}$, Ni^{2+} , Co^{2+}) of schiff base ligand 1-(5-(4-fluorophenyl)isoxazol-3-ylimino)methyl)napthalen-2-ol (L^1) (left) and (2-(5-(4-fluorophenyl)isoxazol-3-ylimino)methyl)-4-methylphenol (L^2) (right) (Ramesh et al., 2020).

6. Conclusion

Schiff base metal complexes are important candidate due to their several biological applications. Advancement of Schiff base-metal complexes towards clinical trials has improved acceptance of the complexes as metal based drugs via pharmaceutical industry and supports further research in this innovative field. In this review, DNA binding and cleavage activity of some metal complexes have been discussed. This review reveals that transition metal ion complexes of Schiff base metal ion might be suitable approaches for the development of novel drugs for medicinal treatment of severe diseases which are challenging to cure by conventional methods. Metal complexes provided new opportunities due to its particular properties in biological field. In this way, these Schiff base metal complexes offer

new opportunities to design and synthesize new drug molecules with improved mechanism of action and trends for the treatment of various diseases.

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