Formazan-Based Metal Complexes for Applications in Resistive Switching and Electrocatalysis

A Thesis submitted by

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Summary and Conclusions

This thesis focuses on the development of synthetic procedures of formazan ligands and their corresponding metal complexes. The redox-active nature of these complexes based on formazanate ligands was demonstrated using electrochemical methods. These complexes were primarily characterized with SC-XRD along with various spectroscopic techniques. Complexes were further utilized for applications in diverse domains, such as memory devices, antimicrobial agents, and cathode material in H_2O_2 fuel cells. The thesis work is summarized in the following section.

8.1 SUMMARY

Chapter 1 provides a comprehensive introduction to redox-active ligands from both natural and artificial systems. In the case of artificial redox-active ligands, several selected examples show an important concept that redox equivalents can be stored in redox-active ligands first and subsequently used for a chemical transformation. The redox-active formazan system serves as an illustrative example of this phenomenon, and its metal complexes play a significant role in advancing research in several fields.

Chapter 2 discusses the various characterization techniques used in this work.

Chapter 3 demonstrates the synthesis of an ionic organotin complex **1** containing redox-active 1,5-Diphenyl-3-(2-pyridyl)formazan ligand, which is structurally characterized by a single-crystal X-ray diffraction technique. Memory device with sandwich structure Al/Complex **1**/ITO was fabricated using complex **1** as the active layer. The device intriguingly displayed non-volatile write once-read many (WORM) memory behavior, with a high switching on-off ratio of 10^4 and retention time of 4.5×10^4 s.

Chapter 4 discusses the synthesis and characterization of a novel distorted octahedral bis(formazanate) Zn(II) complex, **2,** based on a 3-cyano substituted formazan ligand**.** This was also used as an active material for fabricating memory devices with sandwich structure Ag/Complex **2**/TiO_2/FTO. The device interestingly demonstrated non-volatile RRAM memory behavior, with a high switching on-off ratio of $>10^3$ and retention time of 2×10^3 s, suggesting that formazanate complexes may have potential as RRAM memory materials.

Chapter 5 discusses another novel octahedral complex $[Zn^{II}L1_2]$ (**3**), which was synthesized using the newly prepared benzothiazole substituted redox-active formazan-derived ligand L1H = 1-(benzothiazol-2-yl)-5-(2-benzoyl-4-chlorophenyl)-3-phenyl formazan. Furthermore, the solution-processable complex 6 was utilized as the primary building material for resistive switching memory application. The [FTO/$Zn^{II}L1_2$(**3**)]/Ag RRAM device demonstrates exceptional resistive memory switching properties, with a substantial I_{ON}/I_{OFF} ratio (10^3), low operational V_{SET} and V_{RESET} (0.9 V and -0.75 V) voltages, excellent endurance stability (100 cycles), and decent retention time (more than 2000 seconds). This study also demonstrates the significance of N-aryl substitution in the formazan backbone, which reduces the LUMO energy of the metal complex, leading to excellent performance in resistive switching memory devices.

Chapter 6 discusses the electrocatalytic H_2O_2 reduction by the molecular cathodes prepared by immobilizing the bis(formazanate) Fe(II) complexes, $[Fe^{II}(L2)_2]$ **4**, where L2H = 1-(benzothiazol-2-yl)-5-phenyl-3-(pyren-1-yl)formazan and $[Fe^{II}(L1)_2]$ **5**, where L1H = 1-(benzothiazol-2-yl)-5-(2-benzoyl-4-chlorophenyl)-3-phenyl formazan on the surface of a glassy carbon electrode.

Chapter 7 demonstrates the preparation of a novel distorted square pyramidal mercury complex, [Hg^{II}(L3)Cl] (**6**), based on 3-Cyano-1,5-(quinolin-8-yl)formazan ligand L3H, which was further evaluated for its anti-bacterial activity *in vitro*. Supramolecular analysis of complex **6** revealed a solid-state arrangement featuring diverse intermolecular interactions, including the existence of fascinating Hg–Cl···Hg intermolecular spodium bonds of the order 3.348 Å. Additionally, the formazanate-based mercury(II) complex (**6**) was evaluated for its antibacterial efficacy against Gram-positive (*Bacillus subtilis* and *Staphylococcus aureus*) and Gram-negative (*Escherichia coli* and *Pseudomonas aeruginosa*) bacterial pathogens. Furthermore, an in silico pharmacophore-guided rational drug designing approach was utilized to ascertain the likely therapeutic target of the formazanate-based mercury(II) complex. A proposed molecular mechanism for the bactericidal action of the newly synthesized complex (**6**) has also been proposed based on the *in silico* results.

8.2 CONCLUDING REMARKS

Redox-active ligands are systems that can directly engage in redox transformations during chemical reactions by accepting or giving electrons to or from substrates. By employing this unique characteristic, metal centers that are coordinated by redox-active ligands are able to prevent themselves from reaching unstable oxidation states during chemical redox reactions. Thus, the study of redox-active ligands is currently receiving increased attention due to their capability to replace precious metals with base metals. The ligands described in this work are based on the formazan backbone, which is a nitrogen-rich analogue of well-known β-diketimine ligands. Formazans boast a rich history in chemistry, where deprotonation generates monoanionic chelating N-donor ligands called "formazanates". The modular synthesis of parent formazans provides a straightforward route to formazanate complexes with tunable steric and electronic characteristics. Complexes featuring a coordinated formazanate ligand typically exhibit a narrow HOMO–LUMO gap, resulting in energetically accessible π*-orbitals. This property renders formazanate complexes redox-active, enabling reversible storage of electrons in a ligand-based manner within these compounds. The thesis focuses on metal complexes based on formazanate ligands and uses them to understand their role in various fields, such as memory devices, antibacterial behavior, and electrocatalysis. The findings provided in this thesis provide a solid foundation for future investigations into novel chemistry facilitated by complexes containing redox-active formazanate ligands.

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Appendix I

List of Published Papers:

1. **Birara, S.,** Betal, A., Lama, P., Sahu, S., & Metre, R. K. (2023). WORM type memory device based on ionic organotin complex using 1,5-diphenyl-3-(2-pyridyl)formazan ligand. Journal of Molecular Structure, 1287, 135708.

2. **Birara, S.,** Saini, S., Majumder, M., Lama, P., Tiwari, S. P., & Metre, R. K. (2023). Design and Synthesis of Solution-Processed Redox-Active Bis(Formazanate) Zinc Complex for Resistive SwitchingApplications. Dalton Transactions, 52(48), 18429-18441.

3. **Birara, S.,** Saini, S., Majumder, M., Lama, P., Tiwari, S. P., & Metre, R. K. (2024). Solution-Processable Benzothiazole-Substituted Formazanate Zinc(II) Complex Designed for Robust Resistive Memory Device. Dalton Transactions, 53 (36), 15338-15349.

4. **Birara, S.,** Majumder, M., Metre, R. K. Bis(formazanate) Iron(II) Complexes as Cathode Material for One-Compartment H_2O_2 Fuel Cell. Dalton Transactions, 2025, 54, 4120-4134.

5. **Birara, S.,** Yadav, V. K, Jena A. K, Bhattacharyya, S., Metre, R. K. In Vitro and In Silico Based Mechanistic View of Therapeutic Antimicrobial Potential of Formazanate Based Mercury(II) Complex. ChemPlusChem, 2025, 90, e202400696.

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