ABSTRACT

Studies on synthesis, physicochemical characterization and structural assessment of mixedligand halo and schiff base complexes of Nickel(II), Copper(II) and Zinc(II) incorporating biologically relevant coligands is the focal theme of the work described in the present thesis. The entire matter of the thesis is distributed over five chapters (Chapter I-V). Each chapter is virtually complete in itself including the references. The descriptions of the results of work undertaken for the present Ph.D. research are presented in chapter III through to chapter V. These chapters (III-V) include a short introduction justifying the specific objective of the work followed by a section on Experimental describing the synthesis and then Result and Discussion and finally the relevant references.

The first chapter (Chapter I) dealing with Introduction and Review of Literature provides a background pertaining to the work described in the thesis. The significance, interests and scope of nickel(II), copper(II) and zinc(II) coordination chemistry has been portrayed in this chapter with citations from contemporary literature. Diversity of structures, synthetic procedures and biomimetic relevance of nickel(II), copper(II) and zinc(II) coordination compounds has found particular attention in this Chapter. Halogens, interaction with nickel(II), copper(II) and zinc(II) in the presence of biorelevant N,O-donor coligands in aqueous solution has been set as broad objective of the present Ph.D. research programme. Apart this
interaction, some of the Schiff base ligand with nickel(II), copper(II) and zinc(II) has also been set as broad objective of the present Ph.D. research programme.

In Chapter II, is included the details of instruments used and analytical methods for solid-state characterization of the complexes.

Chapter III, of the thesis is concerned with synthesis, characterization and assessment of structures of mixed- and fluorochloro/bromo complexes of nickel(II) incorporating natural amino acids or peptide as coligands. Also included in this chapter a description of synthesis of nickel(II) and mixed metal (NiZn) complexes of some Schiff bases. The complexes reported herein are of the type

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\begin{align*}
\text{(NH}_4\text{)}_2 [\text{Ni(Blm)}_2\text{F}_3\text{(H}_2\text{O)}] & \quad (1) \\
\text{(NH}_4\text{)} [\text{Ni(Pro)}\text{F}_3\text{(H}_2\text{O)}]_2 & \quad (2) \\
\text{(NH}_4\text{)} [\text{Ni(Thr)}_2\text{F}_3\text{(H}_2\text{O)}] & \quad (3) \\
\text{[Ni(Blm)}_2\text{Cl}_2\text{(H}_2\text{O)}]_2 & \quad (5) \\
\text{(NH}_4\text{)} [\text{Ni(Thr)}_2\text{Cl}_3\text{(H}_2\text{O)}] & \quad (6) \\
\text{(NH}_4\text{)} [\text{Ni(Thim)}_2\text{Br}_3\text{(H}_2\text{O)}] & \quad (7) \\
\text{(NH}_4\text{)} [\text{Ni(Lym)}_2\text{Cl}_3\text{(H}_2\text{O)}] & \quad (8) \\
\text{(NH}_4\text{)} [\text{Ni(Mim)}_2\text{Br}_3\text{(H}_2\text{O)}] & \quad (9) \\
\text{[Ni(L)}_2\text{]} & \quad (10) \\
\text{[Ni(Zn)}_2\text{]} & \quad (11) \\
\text{[Ni(U)(PPh)}_3\text{]} & \quad (12) \\
\text{[Ni(L)}_3\text{]}\text{](OAc)}_2 & \quad (13) \\
\text{[Ni(L)}_4\text{]}\text{](PPPh)}_3 & \quad (14) \\
\text{[Ni(L)}_5\text{]}\text{](HIm)}_2 & \quad (15)
\end{align*}
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Chapter IV, of the thesis presents an account of synthesis, physicochemical characterization of copper(II) complexes involving amino acids, semicarbazide and N-hetero cycles type coligands. Schiff base complexes of copper, and mixed metals (CuZn, CuNi) have been documented. Those reported herein are of the type
The final Chapter V, deals with synthesis, characterization and structural assessment of zinc(II) complexes involving amino acids and N-hetero cycles type coligands. Synthesis of some zinc(II) Schiff base complexes have been incorporated herein. The complexes synthesised are

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\begin{align*}
[NH_4][Cu(Lys)F_3(H_2O)] & \quad (16) & [NH_4][Cu(Thr)F_3(H_2O)] & \quad (17) \\
[NH_4][Cu(Blm)F_3(H_2O)] & \quad (18) & [NH_4][Cu_2(Blm)F_6(H_2O)_2] & \quad (19) \\
[NH_4][Cu(Blm)F_3(H_2O)] & \quad (20) & [NH_4][Cu(Thr)Cl_3(H_2O)] & \quad (21) \\
[NH_4][Cu(Blm)Cl_3(H_2O)] & \quad (22) & [Cu(Sem)Cl_3] & \quad 3H_2O & \quad (23) \\
[NH_4][Cu(Blm)Br_3(H_2O)] & \quad (24) & [Cu(Mlm)Br_3(H_2O)_2] & \quad (25) \\
[Cu(Sem)Br_2] & \quad 4H_2O & [Cu(L_2)_2] & \quad (26) \\
[Cu_2(L_2)_2] & \quad (27) & [Cu Ni(L_2)_2] & \quad (29) \\
[Cu Zn (L_2)_2] & \quad (30) & [Cu(L_3)](OAc)_2 & \quad (31) \\
[Cu (L_3)(Hlm)] & \quad (32) & &
\end{align*}
\]

Room temperature, magnetic moments data are consistent with a mononuclear and binuclear structure. In all, aqueous medium, pH-based strategy, simpler materials and milder reaction conditions are redeeming feature of synthesis described in the present thesis.

A summary describing the research highlights has been appended at the end. Part of the work described in Chapter III, IV and V have been published in AU journal of Science and Technology and the rest are being compiled for publication.