Abstract

The main objectives of this thesis are the synthesis Schiff base coordinated polynuclear copper(II) complexes and investigate their potential application in molecular magnetism and in the area of biochemistry. Since multidentate Schiff base ligands have both bridging and chelating binding modes with metals, they often form polynuclear complexes with transition metal ions without any co-ligands. In addition to this they also form polynuclear transition metal complex in combination with various co-ligands. The polynuclear copper(II) complexes were synthesized adopting the following two methods:

i) Using multidentate Schiff base ligand containing at least two hydroxyl groups with Cu(II) salts.

ii) Using multidentate Schiff base ligand in combination with a linear dicarboxylate.

The synthesized complexes are characterized by elemental analysis, IR, NMR spectroscopy, ESI-mass, X-ray single crystal structure determination and low-temperature magnetic measurement. Variable temperature magnetic measurements were carried out and the results obtained have been correlated with their corresponding structural features. This thesis also presented the study of the interaction of polynuclear copper(II) complexes with calf-thymus DNA and serum albumins (bovine serum albumin / human serum albumin). Modes of interaction of complexes with CT-DNA and serum albumins have been explored by molecular docking studies. So, these works might be proved beneficial in the future to cater the demands of the smart materials in the various fields like material chemistry, medicinal chemistry etc. and also enrich the family of Schiff base coordinated polynuclear copper(II) complexes.

Chapter 1 contains general introduction and literature survey about 3d metal coordination compounds and their potential applications, such as magnetic, fluorescence and biological activity.

Chapter 2, describes synthesis and characterization of three novel tetranuclear copper(II) complexes namely $[Cu_4(L^1)_4]\cdot(dmf)$ (**1**), $[Cu_4(L^1)_4]$ (**2**) and $[Cu_4(L^2)_2(HL^2)_2(H_2O)_2]\cdot 2(ClO_4)\cdot 6(H_2O)$ (**3**) (H_2L^1, (*E*)-2-((1-hydroxybutan-2-ylimino)methyl)phenol; H_2L^2, (E)-2-((1-hydroxybutan-2-ylimino)methyl)-6-methoxyphenol)). The complexes were synthesised by the reaction of copper(II) perchlorate and the tridentate Schiff base ligands. Complexes **1** and **2** possess face-sharing dicubane core structure, on the other hand complex **3** has double open cubane core structure. Variable temperature magnetic susceptibility measurements in the range 2-300 K indicate an overall weak antiferromagnetic exchange coupling in all complexes.

Chapter 3, present two copper(II) complexes, $[Cu_4(L)_2(HL)_2(H_2O)_2]\cdot 2(ClO_4)\cdot 2(H_2O)\cdot DMF$ (**1**) and $[Cu_4(L)_2(HL)_2(H_2O)_2]\cdot(tp)$ (**2**) [H_2L = 2-ethoxy-6-[(1-hydroxymethyl-propylimino)-methyl]-phenol; tp = terephthalate] which were synthesized and characterized by single crystal X-ray diffraction and spectroscopic studies. The structural determination reveals that both the complexes are tetranuclear with double-open-cubane like core framework. Interactions of complexes with the calf thymus DNA (CT-DNA) and serum albumins were investigated using electronic absorption and fluorescence spectroscopic techniques.

Chapter 4, represent synthesis and characteization of Cu(II) complexes $[Cu_4(L)_2(HL)_2(H_2O)_2]\cdot 2(pv)$ (**1**) and $[Cu_4(L)_2(HL)_2(H_2O)_2]\cdot(ssal)$ (**2**) [H_2L = 2-Ethoxy-6-[(1-hydroxymethyl-propylimino)-methyl]-phenol; pv = pivalate; ssal = 2-Hydroxy-5-sulfosalicylate].

Both the complexes are tetranuclear with double open cubane core framework. C-H…π interactions results the formation of 1D supramolecular structure for both the complexes. The interactions of complexes with the calf thymus DNA, bovine serum albumin (BSA) and human serum albumin (HSA) were studied using UV-vis absorption and fluorescence spectroscopic techniques. Molecular docking technique has been used to determine the mode of interaction of complexes with CT-DNA and serum albumins.

Chapter 5, reports the synthesis of two 1D polynuclear copper(II) compounds$\{[Cu_2(HL^1)_2(fum)]\cdot(H_2O)\cdot(MeOH)\}_n$(**1**) and $\{[Cu_2(L^2)_2(tp)]\cdot(H_2O)\}_n$ (**2**)(fum = fumarate ; tp = terephthalate) using alkoxo, hydroxo, phenoxo and imine donor Schiff bases [(E)-2-((1-hydroxybutan-2-ylimino)methyl)phenol] (H_2L^1) and [(E)-2-((1-hydroxybutan-2-ylimino)methyl)-6-methoxyphenol] (H_2L^2). Structure determination reveals that the complexes **1** and **2** crystallize in the monoclinic system with space group $P2_1/n$ and Pn, respectively. Variable temperature magnetic property study indicates overall antiferromagnetic exchange coupling in both the complexes. The interaction of complexes with calf thymus DNA (CT-DNA) and bovine / human serum albumins were studied using electronic absorption and fluorescence spectroscopic techniques.

Chapter 6, contain synthesis and characteization of two copper(II) complexes namely $[Cu_4(L^1)_4]\cdot0.5(H_2O)$ (**1**) and $[Cu_4(L^2)_2(HL^2)_2(H_2O)_2](sq)\cdot2(H_2O)$ (**2**) (H_2L^1= [(E)-2-((1-hydroxybutan-2-ylimino)methyl)phenol], H_2L^2 =[(E)-2-((1-hydroxybutan-2-ylimino)methyl)-6-methoxyphenol], sq = squarate and tp = terephthalate ion).The structural determination reveals that complex **1** crystallizes in the triclinic system with space group $P\bar{1}$, whereas complexes **2** crystallize in the monoclinic system with space group $P2_1/n$. Both **1** and **2** are tetranuclear species with Cu_4O_4 close cubane core and double-open cubane like core structure, respectively.

Variable temperature magnetic property study indicates overall antiferromagnetic exchange coupling in both complexes. The PHI program was used to study their magnetic behavior. The Hamiltonians of type $H = - J_1 (S_1S_2 + S_1S_4 + S_2S_3 + S_3S_4) - J_2 (S_1S_3 + S_2S_4)$ and $H = - J_1 (S_1S_3 + S_2S_4) - J_2 (S_1S_2 + S_3S_4) - J_3S_1S_4$ were used to study magnetic behavior of **1** and **2**, respectively, and good agreement between the experimental and simulated results were found by using the parameters: $g = 2.14$, $J_1 = -20.2$ cm^{-1} and $J_2 = -1.7$ cm^{-1} for **1**, and $g_1 = 2.14$, $g_2 = 2.12$, $J_1 = -54.8$ cm^{-1}, $J_2 = -15.9$ cm^{-1} and $J_3 = 0$ cm^{-1} for **2**.