Abstract

The fundamental goal of the thesis is the synthesis of polynuclear copper(II) and cobalt(II/III) complexes by using multidentate N, O-donor Schiff base ligand and aromatic dicarboxylate as co-ligand and study of their potential application in the area of magnetism, catalysis and different biological processes.

Chapter I deals with general introduction on Co(II/III) and Cu(II) coordination compounds of Schiff base ligands and their various properties (magnetic properties, catecholase activities, serum albumin interaction, CT-DNA interactions). It also describes the scope of this thesis.

Chapter II comprises the synthesis of two Co^{II}-Co^{III} mixed-valance complexes of molecular formulas $\{[Co_2(H_2L)_2(H_2O)_2][Co_2(H_2L)_2(H_2O)(m\text{-phth})]\cdot 8(H_2O)\}$ (**1**) and $\{[Co_4(H_2L)_4(H_2O)_2(ppda)]\cdot 2(dmf)\cdot 3.2(H_2O)\}$ (**2**) [H_2L^{2-} = 2-[(2-hydroxy-3-methoxybenzylidene)amino]-2-(hydroxymethyl)propane-1,3-diolato, *m*-phth = 1,3-benzenedicarboxylate, ppda = 1,4-phenylenediacrylate, dmf = N,N-dimethylformamide] and characterized by single-crystal X-ray diffraction and magnetic studies at low temperature. The structural determination reveals that complex **1** is composed of dinuclear ion pairs, namely, a cationic $[Co_2(H_2L)_2(H_2O)_2]^+$ (**1^+**) and an anionic $[Co_2(H_2L)_2(H_2O)(m\text{-phth})]^-$ (**1^-**) unit. In each of these ions, the Co^{II} and Co^{III} centers present distorted octahedral geometries. Compound **2** is a centrosymmetric tetranuclear complex comprising two symmetry-related dinuclear Co^{II}-Co^{III} units bridged by the ppda anions. Alternating current/direct current (ac/dc) magnetic studies revealed that the individual Co^{II}-Co^{III} unit exhibits field-induced slow magnetic relaxation consistent with single-ion magnet (SIM) behavior. Ab initio NEVPT2 calculations confirm large zero-field splitting (zfs) coming from a first-order spin-orbit coupling (SOC) in both complexes (D = -62.4, -95.8, and –101.9 cm^{-1} and E/D = 0.219, 0.216, and 0.234 for **1^+**, **1^-** and **2**, respectively).

Chapter III deals with the synthesis and structural characterization of two novel tetranuclear closed-cubane like core framework complexes $[Cu_4(L^1)_4]\cdot3(H_2O)$ (**1**) and $[Cu_4(H_2L^2)_4(H_2O)_4]$ (**2**) (H_2L^1 = (E)-2-((1-hydroxybutan-2-ylimino)methyl)phenol; H_4L^2 = 2-((2-hydroxy-3-methoxybenzylidene)amino)-2-hydroxymethylpropane-1,3-diol). Magnetic susceptibility measurements indicate an overall weak antiferromagnetic exchange coupling in **1**, while ferromagnetic exchange coupling in **2**. In agreement with their closed-cubane structure, the magnetic behavior of the two complexes have been studied by employing the isotropic spin Hamiltonian of type $H=J_1 (S_1S_3 + S_1S_4 + S_2S_3 + S_2S_4) - J_2 (S_1S_2 + S_3S_4)$ (J_1 describes the magnetic exchange coupling between the four Cu(II) pairs with short Cu···Cu distances, while J_2 characterizes the magnetic exchange coupling between the remaining two intermetallic pairs with long distances). The PHI program was used to study their magnetic behavior. A good agreement between the experimental and fitted curves was found with the following parameters: $g = 2.14$, $J_1 = -20.3$ cm^{-1} and $J_2 = 0$ cm^{-1} for **1** and $g = 2.10$, $J_1 = 101.1$ cm^{-1} and $J_2 = -51.5$ cm^{-1} for **2**.

Chapter IV presents the synthesis of two novel copper(II) complexes, $[Cu_4(L)_2(LH)_2(H_2O)_2]_2(NO_3)_2.(pydc).9H_2O$ (**1**) and $\{[Cu_4(L)_2(LH)_2(H_2O)_2(ppda)].5H_2O\}_n$ (**2**) [H_2L = 2-[(2-hydroxy-ethylimino)-methyl]-6-methoxy-phenol, pydc = pyridine-3,5-dicarboxylate, ppda = phenylene-1,4-diacrylate]. These two complexes have been characterized by X-ray single crystal diffraction analysis and low temperature magnetic study. The structural determination reveals for complex **1** a tetranuclear species exhibiting a double-open cubane like core framework, whereas use of ppda anions results 1D coordination polymer where tetranuclear double-open cubane cores are connected by bridging ppda ligands. In both the complexes, hydrogen bonding interactions lead to 3D supramolecular structures. Low temperature magnetic study indicates antiferromagnetic coupling in both the complexes. A model based on an effective square tetramer of Heisenberg spins was used to determine exchange strengths of 174(2) K for **1** and 107.4(4) K for **2**.

Chapter V describes the synthesis and characterization of two tetranuclear Schiff base copper(II) complexes, namely $[Cu_4(L)_2(LH)_2(H_2O)_2](ClO_4)_2 \cdot 3H_2O$ (**1**) and $[Cu_4(L)_2(LH)_2(H_2O)_2](ClO_4) \cdot (tp)_{0.5} \cdot 3H_2O$ (**2**) (where H_2L = 2-[(2-hydroxy-ethylimino)-methyl]-6-methoxy-phenol, tp = terephthalate), by X-ray single crystal diffraction. Both complexes **1** and **2** are comprised of structurally similar tetranuclear cationic $[Cu_4(L)_2(LH)_2(H_2O)_2]^{2+}$ species with a double open cubane core, in which two metal centers possess a square pyramidal environment and the other two exhibit a slightly distorted octahedral coordination geometry. The interaction of complexes **1** and **2** with calf thymus DNA (CT-DNA) was investigated using electronic absorption and fluorescence studies, and the results showed that the complexes interact with CT-DNA with the related intrinsic binding constants (K_{ib}) of 1.8×10^6 and 1.1×10^7 L mol^{-1} for **1** and **2**, respectively. Their interactions with bovine serum albumin (BSA) and human serum albumin (HSA) were also investigated and spectroscopic techniques showed that both complexes interact with these proteins through a ground state association process. Using 3,5-di-tertbutylcatechol (3,5-DTBC) as a model substrate, both complexes show catecholase-like activity, being able to oxidase 3,5-DTBC to 3,5-di-tertbutylquinone (3,5-DTBQ) in the presence of oxygen.