

The principles of coordination chemistry e.g. ligand field theory constitute a common ground for molecular magnetism, biomimetics and bioinspired chemistry. The subject of *molecular magnetism* is the center of this thesis. Summarily, this thesis mainly deals with the magneto-structural studies of homo- and heteropolynuclear metal complexes, with particular emphasis on the investigations of different exchange pathways. Different spectroscopic techniques (viz. MS, IR, NMR, UV-VIS, SQUID, EPR, MCD, etc) have been used to provide a complete picture as possible. This work is divided into seven chapters. The first chapter gives an introduction relevant to this work, considering the background of "*Molecular Magnetism*" and the importance of the *exchange coupled* polynuclear complexes in "*molecular magnetism*" and *magnetic molecular materials*. The importance of hydroxyl- or oxime-group containing ligands as backbones for polynuclear complexes due to their versatility at bonding modes have been discussed. Basic principle of MCD has also been discussed here. In Chapter 2 the use of hydroxyl-group containing ligands to influence the nuclearity and topology of metal complexes is reported. Some other interesting developments regarding the magneto-structural chemistry of complexes incorporating this ligand are discussed. The aggregation of soft metal centers to form covalently bonded clusters is well known. Hard metal cations do not readily form metal-metal bonds, and usually require bridging ligands such as carboxylate, oxide, or hydroxide ligands to induce aggregation. Herein we report two interesting examples of metal–ligand frameworks which can be successfully self-assembled about an alkali metal cation template. Polynuclear complexes with oximate bridges have been reported, however the coexistence of multiple bridging pathways preclude clear analysis of the magnetic coupling via oximate bridges only. To clarify the nature of exchange interactions via oximate ligands, the synthesis of new materials was necessary. Working towards this goal, the singly oximate-bridged $[\text{Mn}^{\text{III}}]_n$ complex has been successfully synthesized and is discussed in Chapter 3. Chapter 4 concerns the synthesis and characterization of a ferromagnetically coupled dinuclear ferric complex. Though the spin-polarization mechanism is well known Abstract for organic polyradical systems, it has received limited attention in case of metal coordinated systems. This system has also been studied using DFT. In Chapter 5 the synthesis and characterization of a valence-trapped tetranuclear $[\text{V}(\text{III})\text{V}(\text{IV})]_2$ -complex, a rare example of a mixed-valent vanadium cluster without any carboxylate or phosphate ligands is reported. Finally, in Chapter 6 a series of dinuclear homo- and heteropolynuclear complexes using *N*-methylimidazolealldoxime as a bridging group are reported. We have previously reported such series of complexes with pyridinealldoxime ligands. In this chapter we also show how this allows straightforward comparison of magnetic and coordination properties between complexes of 1-methyl-2-imidazolealldoxime and pyridinealldoxime ligands with 3d-transition metals. MCD is an important analytical tool to investigate the geometric and electronic structures of transition metal complexes. Together with magnetostructural studies, Chapter 6 also concerns the MCD studies of $\text{Fe}^{\text{III}}\text{Ni}^{\text{II}}$, $\text{Fe}^{\text{III}}\text{Zn}^{\text{II}}$ and $\text{Ga}^{\text{III}}\text{Ni}^{\text{II}}$ complexes with the ground state $S = 3/2$, $5/2$ and 1, respectively.