OUTLINE OF THE THESIS

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 describes *exchange-coupled* homo and heteropolynuclear complexes, containing different paramagnetic metal ions, with particular emphasis on the interactions of spin carriers based on different *topological* approach with irregular *spin state structures* towards building *high-spin* molecules. These polynuclear complexes described here are characterized structurally and spectroscopically so that magnetostructural *correlations* can be made.

This work is divided into eight 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 oxime ligands as backbones for polynuclear complexes due to their versatility at bonding modes is discussed. A few examples of well characterized *high spin* molecules, relevant to this thesis, are reviewed.

The second chapter is concerned with the synthesis, characterization and magnetostructural study of *exchange coupled* trinuclear oximate complexes. It is to be mentioned here that new exchange pathways can be expected for heteropolynuclear complexes where unusual sets of magnetic orbitals can be made to overlap with each other and hence investigations of a series of heteropolynuclear complexes might be more informative in comparison to those of homometal complexes. Three trinuclear complexes, $\mathbf{Ni^{II}Mn^{III}Ni^{II}}$ **1**, $\mathbf{Ni^{II}Cr^{III}Ni^{II}}$ **2** and $\mathbf{Ni^{II}_3}$ **3** based on (pyridine-2-aldoximato)nickel(II) units are described. Two of them, **1** and **2**, contain metal-centers in linear arrangement, as is revealed by X-ray diffraction. Complex **3** is a homonuclear complex in which the three nickel(II) centers are disposed in a triangular fashion. The compounds were characterized by various physical methods including cyclic voltammetric and variable-temperature (2–290 K) susceptibility measurements. Complexes **1** and **3** display antiferromagnetic exchange coupling of the neighboring metal centers, while weak ferromagnetic spin exchange between the adjacent Ni^{II} and Cr^{III} ions in **2** is observed. The experimental magnetic data were simulated by using appropriate models.

The third chapter presents linear tetranuclear "*homo and heteropolymetallates*" constructed using a dinucleating oxime ligand. One dinuclear and four tetranuclear

complexes, **$Mn^{II}Mn^{II}$ 4, $Mn^{III}Mn^{II}Mn^{II}Mn^{III}$ 5, $Mn^{IV}Mn^{II}Mn^{II}Mn^{IV}$ 6, $Fe^{III}Mn^{II}Mn^{II}Fe^{III}$ 7** and **$Cr^{III}Mn^{II}Mn^{II}Cr^{III}$ 8** based on (2,6-diformyl-4 methyl phenoldioximato)manganese(II) units are described. All of them contain metal-centers in linear arrangement, as is revealed by X-ray diffraction. The compounds were characterized by various physical methods including cyclic voltammetric and variable-temperature (2–290 K) susceptibility measurements. Complexes display overall antiferromagnetic exchange coupling with extremely low-lying states.

The fourth and fifth chapters discuss the building up of high spin polynuclear complexes based on different *molecular topology* such as, butterfly, star-shaped etc, and a "parallel spin coupled" system using "accidental ferromagnetism" and "planned ferromagnetism" both governed by the common principle of orthogonal orbital overlap. It also discusses *irregular spin state structures* due to *spin frustration* or *competing exchange interaction.* Two tetranuclear complexes, **$Fe^{III}_2Cu^{II}_2$ 9**, **$Cu^{II}_2Cr^{III}_2$ 10** based on (2,6-diacetyl pyridinealdoximato)copper(II) units and $Me_3TacnMX_3$ (where M = Fe(III), Cr(III) and X = Cl or Br) are described. Both of them, **9** and **10**, contain metal-centers disposed in "butterfly" fashion with M(III) as the "wing" and Cu(II) as the "body", as is revealed by X-ray diffraction. The compounds were characterized by various physical methods including variable-temperature (2–290 K) susceptibility and variable-temperature variable-field (VTVH) magnetic measurements. The experimental magnetic data were simulated by using appropriate models Complexes **9** and **10** display antiferromagnetic exchange coupling of the neighboring metal centers, due to the "spin-frustration" or more precisely competing exchange interactions between the spin carriers complex **10** exhibits irregular spin state structure with $S_T = 2$ ground state. While strong wing-body interactions over body-body interaction, stabilizes $S_T = 4$ ground state in complex **9**.

Two tetranuclear complexes, **Mn^{II}_4 11**, **Mn^{III}_4 12** based on salicylaldoxime ligand are described. One of them, **11** contains metal-centers in "star-shaped" arrangement while the complex **12** in which the four manganese(III) centers are disposed in a tetrahedral fashion, as is revealed by X-ray diffraction. The compounds were characterized by various physical methods including variable-temperature (2–290 K) susceptibility and variable-temperature variable-field (VTVH) magnetic measurements. The experimental magnetic data were simulated by using appropriate models Complexes **11** and **12** display weak ferromagnetic exchange coupling of the neighboring metal centers, and yield high-spin $S_T = 10$ and $S_T = 8$ ground states for the complexes **11** and **12** respectively.

Also hexa-and nonanuclear complexes have been synthesized and are described in chapters six and seven. The hexanuclear complexes, composed of two edge-sharing triangular units, are also subjected to magnetostructural studies as described in chapter five, while sixth chapter describes two rare examples of nonanuclear Ni(II) and Cu(II) complexes**.** Two nonanuclear complexes, $\mathbf{Ni^{II}_9}$ **16**, $\mathbf{Cu^{II}_9}$ **17** based on (pyridine-2-aldoximato)nickel(II) unit and N,N'-(2-Hydroxypropane-1,3-diyl)bis(benzoylacetoneimine) respectively are described. Both of them, **16** and **17**, contain two irregular tetrahedra connected to a centrally placed M(II) ions, as is revealed by X-ray diffraction. The compounds were characterized by various physical methods including variable-temperature (2–290 K) susceptibility measurements and variable-temperature variable-field (VTVH) magnetic measurements. Complexes **16** and **17** display antiferromagnetic exchange coupling of the neighbouring metal centers. The experimental magnetic data were simulated by using appropriate models.