PREFACE

Schiff base complexes of manganese(III) are well known for the variety of the structures formed and associated magnetic properties as well as catalytic applications. Of particular interest is the role of Mn(III) as well as other oxidation states of manganese in biological electron transfer. The five coordinate complexes of the general formula Mn(SB)X where SB is a tetradentate Schiff base and X is an anionic ligand often become six-coordinated through coordination with solvent, formation of 1D-chain polymers via bridging through X, or dimerisation via bridging through the phenoxo-oxygen. Additional non-covalent interactions may lead to formation of networks in the solid state. Dimerisation and polymerisation are of more widespread occurrence when X is a pseudohalide like azide or thiocyanate. The present thesis extends the earlier work done in the research group on the pseudohalide complexes.

As part of the present study, several phenoxo-bridged dinuclear complexes as well as 1D-chain complexes have been prepared using conventional synthetic procedures, crystallized and characterized using X-ray crystallography. In some cases polymorphs have been identified which includes the first Mn(III) 1,1-azide bridged chain. In many cases detailed magnetic studies have also been made. The study of molecular magnetism has undergone rapid developments during the past three decades starting with magneto-structural correlations made by measuring exchange coupling parameters for a variety of transition metal complexes and culminating in the characterization of high spin ground states and single molecule

magnetism(SMM). Along with bio-inorganic model building, realization of high spin ground states with high nuclearity manganese complexes has provided some of the motivation for research in manganese coordination chemistry. In recent times, SMM has been observed for some phenoxo-bridged Mn(III) dimers as well. In the present study also a few such ferromagnetic dinuclear complexes exhibiting slow relaxation of magnetization at low temperatures (<10 K) have been obtained. There are also cases in which weak interactions in the crystal lattice provided significant pathways for magnetic exchange.

Part of the work being reported in this thesis have been communicated for publication:

1. Synthesis, Crystal Structure and Magnetic Properties of Dimeric Mn^{III} Schiff BaseComplexes Including Pseudohalide Ligands. Ferromagnetic Interactions through Phenoxo Bridges and Single Molecule Magnetism. G. Bhargavi, M. V. Rajasekharan, J.-P. Costes and J.-P. Tuchagues. (in press *Polyhedron*)
2. Antiferromagnetic interactions through phenoxo bridges and lattice water. Synthesis, structure, and magnetic properties of new Mn(III) Schiff base complexes in combination with thiocyanate ligand. G. Bhargavi, M. V. Rajasekharan, and J.-P. Tuchagues. (Communicated to *Inorg. Chem. Acta*)