

ABSTRACT

Crystal engineering provides a platform to understand crystal packing of a series of coordination polymers (CPs) employing data mining and retroanalysis. Rationalization of a structural landscape enables one to interpret self-assembly of soluble molecular species condensing into a crystal. Thus, one could design new and functional CPs for various applications providing a path to comprehend the diverse nature of extended metal-ligand architectures. In addition, the tunable and tailorable crystalline structures would become model systems to study synthesis-structure-property with enhanced phenomenological understanding. Crystallization of new CPs from solution is still difficult to predict as the self-assembly processes employed are strongly influenced by subtle variables like solvent, counterion and stoichiometry of the reactants apart from pH and temperature. Among these, solvent molecules could compete for coordination with metal exerting a significant effect on the outcome of the condensed product. Frequently solvent molecules appear as terminal co-ligands in the scaffold which further regulate the formation of the framework during self-assembly. In a few cases, the solvent molecules could occupy pores or empty spaces; these are referred as lattice solvents. Out of numerous applications foreseen for CPs, magnetic properties are of special interest. Synthetic and theoretical chemists have been looking for polynuclear coordination complex based solids containing transition metal ion(s) in intramolecular spin communication as a way to advance new generation of magnetic materials. A major challenge, however, is to effectively control interactions between magnetic centers in the engineered crystal. In this context, manganese carboxylates are ideal candidates as the metal occurs in various oxidation states (+2 to +4 with $S=5/2$ to $3/2$ respectively) and the metal-carboxylate linkages provide diverse frameworks. Manganese(II) compounds in the high spin ground state ($S=5/2$) are particularly important due to the possibility of strong exchange interaction between $3d$ -electrons.

The magnetic centers with varying unpaired electrons provide a variety of magnetic ordering - spin frustrated multiferroics to single molecule magnetism(SMM). Our lab has been employing a crystal engineering approach to crystallize high nuclear manganese clusters in various polar aprotic/protic solvents. One of our objectives is to rationalize the varied coordination assemblies and study the effect of carboxylates on spin-exchange interactions. In this work, we present our approach to the structural design of new manganese carboxylate coordination polymers, as well as the influence of noncovalent interactions, particularly coordination and H-bonding forces on the overall supramolecular assembly and its magnetic behavior in Chapters II-VI and Appendix I.

Chapter I provides a brief account of our literature survey on the crystal engineering of manganese(II) aromatic dicarboxylate based coordination polymers as well as motivation for the present work. Chapter II discusses the crystallization of manganese(II) with the flexible dicarboxylate, benzophenone-4,4'-dicarboxylic acid (*4,4'-H₂bpdC*) under varying solvothermal condition in different aprotic solvents (DMF, DMA and DMSO). The crystal packing of the three isostructural manganese(II) benzophenone-4,4'-dicarboxylate based CPs was greatly influenced through hydrogen bonding exerted by the coordinated solvent molecule (H₂O, DMF or DMSO) occupying the apical position. Low-temperature antiferromagnetic interactions arising in these solids correlate with the variation in the packing of the layers as confirmed by theoretical calculations. Chapter III examines the influence of N-donor based auxiliary ligands in effecting the structural diversity of the system Mn(II)-*4,4'-H₂bpdC*-solvent. The auxiliary ligands, were intended to restrict manganese coordination sites thereby controlling the metal-carboxylate network. Chapter IV addresses how the structural architectures reported in Chapters II and III, vary when a positional isomer of dicarboxylate, such as benzophenone-2,4'-dicarboxylate (*2,4'-bpdC*) is used. Chapter V reports how crystallization is influenced when we reacted methyl substituted

2,2'-*bipy* and *phen* (Chapters III and IV) with the most celebrated rigid ligands, 1,4-benzene dicarboxylic acid (*H₂bdc*) and 2,6-naphthalene dicarboxylic acid (*H₂nda*). Magnetic property of all the manganese dicarboxylates reported in this thesis showed antiferromagnetic interactions at low temperatures. We have made an attempt to correlate magnetic property with crystal structure. Chapter VI discusses nucleation and crystal packing of all crystals reported here in terms of supramolecular assembly of soluble molecules at supersaturation. Our work demonstrates 1:1 manganese aromatic dicarboxylate is the major building block that eventually condenses into a crystal with a defined stoichiometry. Chapter VII provides a brief summary of the results obtained in this study and concludes highlighting future directions.