Synthesis and Characterization of Three Two-dimensional Manganese Coordination Polymers

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To model the active sites of dimetallic hydrolases, we have recently synthesized and characterized 1, in which the bridging water is stabilized by ancillary intramolecular hydrogen bonds, and N represents a monodentate N-donor ligand such as imidazole(Im) or benzimidazole(BzIm)[1]. It was shown by others that the compounds similar to 1 can be synthesized if N-donor is 4-methylpyridine[2].

![Diagram 1: The structure of 1.](image)

1 demonstrates nicely how a water molecule can be picked up and activated by a dimetallic site for the hydrolysis function. The major drawback of 1, however, is that it tends to dissociate into monomers in solution, making it impossible to study the catalytic behaviors of 1 in hydrolytic reaction.

There seem two approaches to stabilize the assembly in 1. The first is to stabilize each dimer by chelating all ligands other than the water site. This will allow the whole dimer maintaining intact during the water binding, activation, and hydrolysis processes. The second approach is to "network" the dimers into a polymer-like supramolecular structure through two-armed N-donor ligands, making it less prone to dissociation.

![Diagram 2: Stabilization of 1.](image)

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To test the second approach, we tried to use 4,4'-bipyridine(bpy) and its variants to replace Im or BzIm. To our very surprise, instead of the networked dimers with bridging aqua, two-dimensional Mn(II) polymers were obtained, in which the backbones of linear chains were formed by Mn(II) and the two-armed N-donor ligand and the chains were interconnected by carboxylate ligands[3].

Three such Mn(II) coordination polymers were obtained and characterized. They are \([\text{Mn(μ-bpy)(μ-OBz)}_2]_n\), \([\text{Mn}_2(\text{μ-bpy})_2(\text{μ-OAc})_2(η^1\text{-OAc})_2]_n\), 3, and \([\text{Mn(μ-bis(bpy)Et)(OBz)}_2(\text{HOMe})_2]_n\), 4, respectively. The coordination spheres of 2 to 4 are given in Fig. 3. Common to all three polymers, each M(II) has a \(\text{N}_2\text{O}_4\) coordination core. The structural parameters are typical to that of divalent Mn. The two-dimensional layouts for one layer of each polymer are given in Fig. 4, which shows clearly the role of the carboxylate ligands in connecting the main chains of polymers.

![Fig. 3. Coordination Core of 2, 3 and 4.](image)

![Fig. 4. Two-dimensional Layouts for One Layer of Polymer Chains](image)