

Two Novel Metal Organic Frameworks of Sn(II) and Pb(II) with Pyridine-2,6-dicarboxylic Acid and 4,4'-Bipyridine: Syntheses, Crystal Structures and Solution Studies

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(Received 24 April 2009, Accepted 3 July 2009)

Two novel compounds with formulae $[\text{Sn}_2(\text{pydcH})_2(\text{H}_2\text{O})_2\text{O}]_n$, **1**, and $(4,4'\text{-bpyH}_2)_{0.5}[\text{Pb}(\text{pydc})_2(4,4'\text{-bpyH})]_n \cdot 4,4'\text{-bpy} \cdot 4\text{H}_2\text{O}$, **2**, were obtained from a one-pot reaction between pyridine-2,6-dicarboxylic acid (pydcH_2) and 4,4'-bipyridine (4,4'-bpy) with corresponding Sn(II) and Pb(II) salts. In compound **1** with a polymeric structure, each Sn(II) atom is six-coordinated by one water molecule, two $(\text{pydcH})^-$ groups and one oxide group resulted in a coordination polymer. Compound **2** has a seven-coordinated environment around Pb(II) atom by two $(\text{pydc})^{2-}$ groups and one (4,4'-bpyH). The anionic complex is balanced by half a $(4,4'\text{-bpyH}_2)^{2+}$ as counter ion. There are four uncoordinated water molecules and one 4,4'-bpy in the crystal lattice. Therefore, in compound **2**, we have neutral, mono- and biprotonated forms of 4,4'-bipyridine, simultaneously. Several interactions including O-H \cdots O, O-H \cdots N and C-H \cdots O hydrogen bonds, ion pairing, C-O \cdots π (O \cdots Cg 3.324(3) Å and 3.381(3) Å in **1** and O \cdots Cg 3.346(4) Å in **2**), C-H \cdots π (C \cdots Cg 3.618(4) Å in **2**), and $\pi\cdots\pi$ stackings (with Cg \cdots Cg distances of 3.613(2) and 3.641 (2) Å in **2**) are present to expand and stabilize the structure. The complexation reactions of bpy and pydc-bpy with Sn²⁺ and Pb²⁺ ions in aqueous solution were investigated by potentiometric pH titrations, and the resulting equilibrium constants and species distributions at various pHs for major formed complexes are described.

Keywords: Pyridine-2,6-dicarboxylic acid, 4,4'-Bipyridine, Sn(II) and Pb(II) complexes, Crystal structures, Solution studies

INTRODUCTION

The rational design and synthesis of 3D architectures as well as molecular recognition are regarded as key aspects of modern coordination chemistry, not only because of their intriguing topologies but also because of their potential applications as functional materials [1]. Dicarboxylate ligands are widely used to assemble supramolecular network

organized by coordination bonds, hydrogen bonds and $\pi\text{-}\pi$ stacking interactions. On the other hand, the functional groups, flexibility, symmetry and configuration of the organic ligands also have significant effect on the structures of the complexes. Furthermore, the auxiliary ligands, such as 2,2'-bpy, 4,4'-bpy and phen (phenanthroline), have obviously great effect on the structures of complexes [2].

In continuation of our research on supramolecular systems, now we have found a certain route to combine a carboxylic acid with an amine to produce some almost water-soluble

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