



Ditopic carboxylate containing zigzag chain polymers with tetrahedral Co(II) and Zn(II) nodes

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ABSTRACT

Two 1D coordination polymers based on tetrahedral cobalt(II) and zinc(II) complex monomers involving terephthalate (1,4-benzenedicarboxylate) dianions as ligand bridges viz., $[\text{Co}(\text{ta})(\text{DMP})_2]_n$ **1** and $[\text{Zn}(\text{ta})(\text{DMP})_2\text{H}_2\text{O}]_n$ **2** (ta = terephthalate, DMP = 3,5-dimethylpyrazole) have been synthesized and characterized by elemental analysis, spectroscopic methods as well as by single crystal X-ray diffraction method. Compounds **1** and **2** are chain polymers wherein the polymeric zigzag chains remain linked through intermolecular hydrogen bonds to give rise to robust 3D network structures. Topological analysis of the structure of **2** reveals an underlying net that can be described as **2C1**. While the solid state UV–vis–NIR spectrum **2** reflects the tetrahedral coordination geometry around Co(II), thermogravimetric studies indicate that this species retains its 3D network up to about 170 °C. The temperature dependence of the magnetic susceptibility of **1** indicates weak antiferromagnetic interaction among the unpaired spins.

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1. Introduction

Self-assembled polymeric coordination complexes or coordination polymers (CPs) formed through the careful selection of metals and multifunctional ligands have generated tremendous interests in the areas of materials chemistry [1]. The uniform pore sizes/environments and very high surface areas possessed by these materials make them advantageous over traditional microporous and mesoporous materials, including zeolites, mesoporous silicas and activated carbon. The inherent porosity and the variety of their structural frameworks of such CPs based on metal-organic compounds render these MOFs very promising in a variety of applications, such as chemical sensing [2], catalysis [3], gas storage and separation [4], drug delivery [5], proton conduction [6], electrochemical action [7], antimicrobial activity [8], luminescence

properties [9] etc.

Yaghi and co-workers have reported several coordination polymers based on *bis*- and *tris*-bidentate carboxylate linkers copolymerized with Zn(II). In these compounds the nodes are rigid metal-carboxylate clusters, which allow the stability of the porous materials. The sorption behaviour of such systems are well studied and indications are that these are efficient and robust materials for gas storage and liquid separation. These studies also have led to the synthesis of several two- and three-dimensional coordination polymers using transition metals with carboxylate and pyridyl ligands, some of which can act as multidentate organic spacers [10]. In effect, organic polycarboxylate anions are some of the most widely used bridging ligands used for designing polynuclear complexes with interesting magnetic [11] and catalytic properties [12].

The use of dicarboxylate spacers continues to be of interest to chemists attempting to construct coordination polymers of various dimensionalities [13]. Many salts of terephthalic acid have been studied from the point of view of using the terephthalato ligand (ta) as a conjugated bridging ligand making itself available for exchange coupling interactions between metal ions carrying unpaired electrons. For example, the polymeric complex $[\text{Cu}(\text{en})(\text{H}_2\text{O})_2(\text{ta})]_n$ has been shown to align antiferromagnetically at low temperatures [14]. The polymers of coordination compounds also may remain associated via non-covalent interactions including hydrogen

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