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Design and construction of two rare aqua bridged copper (II) coordination polymers through mixed ligand strategy: Synthesis, characterization and single crystal X-ray structure determination of $[Cu(2\text{-iodobenzoate})_2(\beta/\gamma\text{-picoline})_2(\mu\text{-}H_2O)]_n$

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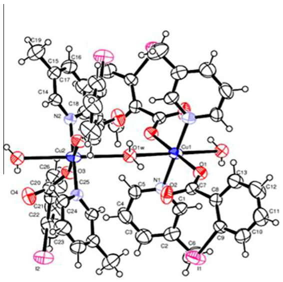
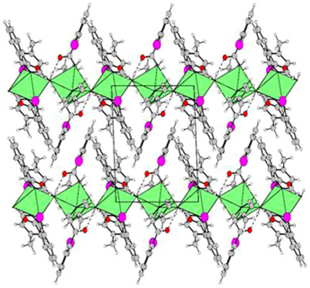
HIGHLIGHTS

- Two rare aqua bridged copper (II) based linear polymers have been synthesized by mixed ligand strategy.
- These polymers were structurally characterized by X-ray crystallography.
- Empty channels have been observed between the linear chains of complexes.
- Non-covalent interactions like O–H···O, C–H···O and C–H···π has been observed.
- The C–H···π interactions leads to the zig-zag patterns of linear chains.

GRAPHICAL ABSTRACT



ORTEP Diagram of complex 1



Aqua bridged zig-zag chains with empty channels

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ABSTRACT

Reaction of hydrated copper (II) 2-iodobenzoate with β/γ-picoline in methanol:water mixture (4:1, v/v) yielded two rare aqua bridged zig-zag polymers $[Cu(2\text{-iodobenzoate})_2(\beta\text{-picoline})_2(\mu\text{-}H_2O)]_n$; **1** and $[Cu(2\text{-iodobenzoate})_2(\gamma\text{-picoline})_2(\mu\text{-}H_2O)]_n$; **2**. The newly synthesized complexes have been characterized by elemental analysis, FT-IR spectroscopy, UV–Vis spectroscopy and single crystal X-ray structure determination. Complex **1** crystallized in monoclinic crystal system with C2/c space group, and complex **2** crystallized in triclinic crystal system with $P\bar{1}$ space group. X-ray structure determination revealed the presence of 1-dimensional chains of constituent molecules running along *a*-axis in both complexes. Water molecules act as bridges between constituent molecules and hence play a crucial role in 1-dimensional chain propagation in zig-zag manner. Empty channels have been observed between the zig-zag chains of complexes. Non-covalent interactions interactions such as O–H···O, C–H···O and C–H···π have been observed, which play a decisive role in the stabilization of crystal lattices in both complexes **1** and **2**.

Introduction

Coordination polymers/metal–organic frameworks are receiving increased interest owing to their intriguing topologies [1–3] and potential applications in gas adsorption, molecular/ionic separation, optics, sensing, catalysis, drug delivery, magnetism and chirality, etc. [4–9]. Coordination polymers have a number of advantages over traditional organic polymers because of their higher thermal stability, flexibility and choice of almost all the elements (metals/metalloids) from the periodic table [10]. A unique

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characteristic of coordination polymers is the preference of a metal ion for a particular geometry depending upon the oxidation state of metal ion and different oxidation states possible for a given metal ion.

It is well known that structure of a coordination polymer is intimately linked with various factors such as geometric requirement of metal ion, organic ligand, nature of counter ion, stoichiometric ratio, method of crystallization, temperature and even solvent system used [11]. Among these factors, organic ligand plays an important role in tuning the structures of a coordination polymer [12,13]. For example, derivatives of pyridine as a model of excellent organic ligand (with strong coordination ability towards various metals) have attracted great interest in the construction of coordination polymers. Generally, one of the successful strategies to synthesize a coordination polymer is to use an appropriate linker that can connect large number of monomer units. There are many linkers [1a,14] (Chart 1) such as pyrazine, bipyridine, terephthalic acid, and 1,3,5-benzenetricarboxylic acid etc. A common feature of many of these linkers is that these molecules are endowed with multiple functional groups that can coordinate from different sites simultaneously to generate polymers of different dimensionalities (Chart 1).

Curiously, in one of our earlier studies we stumbled upon a zigzag copper (II) coordination polymer in which the linker was a water molecule. Our search for similar compounds in the family of aquabis(carboxylato)bis(N-ligands) showed that such complex polymers are rare, only few examples are available [15a]. Structural investigation on [Cu (2-bromobenzoate)$_2$ β/γ-picoline)$_2$ (μ-H_2O)]$_n$ [15b] clearly showed that the polymer formation is invariant to methyl group substitution on to the pyridine ring (i.e. both β/γ picoline are equally effective). Moreover, both these complexes were isostructural (space group $P\bar{1}$) pointing toward the fact that the methyl group substitution at meta/para positions does not alter the structure, the propensity of water molecules to act as a linker is also well preserved in these compounds. It is well known that nature as well as mode(s) of molecular coordination to a metal centre can be influenced by steric constrains of the molecules, but in the present case, positioning of methyl group at meta or para position does not alter the coordination mode. Based on this observation, we put forward another question, can the structure get preserved as water mediated coordination polymer if we substitute bromine with the heaviest halogen (i.e. iodine)? That is, in effect, the structural organization becomes insensitive to the steric bulkiness exerted by ortho substitution of simple aryl carboxylate. If it happens, the mixed ligand methodology that we have adopted for the synthesis of above mentioned two rare aqua bridged complexes can be extended to other substituted arylcarboxylates also. To surmise, we may get augmenting evidence regarding the influence of the ortho substitution toward the coordination polymer formation in this family of complexes. Thus, this paper reports the finding of our studies from the synthesis and structural analysis of aqua bridged copper (II) coordination polymers with 2-iodobenzoate anion. In addition, studies toward these variations of steric bulkiness can evoke theoretical interest regarding the role of rigid nitrogen bases, type and geometrical positioning of suitable substituents at phenyl part of aryl benzoate and even the role of reaction medium (solvent) toward successful synthesis. It is to be noted that the water bridge, considering the hybridisation of oxygen atom (sp^3), the Cu–O–Cu angle, cannot be linear, but it can vary to a large extent to accommodate the crystal lattice requirements (for example, this angle has been widened to ~157° in previously reported complexes, [15b]). Hence the polymer cannot be a linear one, but tends to be in zig-zag form, with a variable zigzaggedness. This study also will establish the role of steric bulkiness on Cu–O–Cu angle variation and the extent of linearity attained by the polymer. Such understanding can open a window for the synthesis of large number of rare aqua bridged copper (II) complexes based on mixed ligand synthetic strategy.

Experimental

Material and instruments

Analytical grade reagents were used throughout this work without any further purification. Carbon, Hydrogen and Nitrogen were estimated micro analytically by automatic Perkin Elmer 2400 CHN element analyzer and copper was determined by standard literature method [16]. Fourier transform infrared spectra were recorded (neat) on PERKIN ELMER SPECTRUM RX FT-IR system. UV–visible spectra were recorded using HITACHI 330 SPECTROPHOTOMETER.

Synthesis

Synthesis of [Cu (2-iodobenzoate)$_2$(β-picoline)$_2$ (μ-H_2O)]$_n$ (1)

0.50 g $CuSO_4 \cdot 5H_2O$ (2 mmol) was dissolved in 10 mL of distilled water. Sodium salt of 2-iodobenzoic acid was prepared in situ by dissolving 0.16 g (4 mmol) of NaOH and 0.99 g (4 mmol) of 2-iodo benzoic acid in minimum amount of water. On mixing the two solutions, precipitated product of copper (II) 2-iodobenzoate was obtained immediately. The precipitated product was filtered through a fine filter paper, washed with water followed by methanol and dried at room temperature (yield 85%). Hydrated copper (II) 2-iodobenzoate was then suspended in methanol–water mixture (4:1, v/v) and β-picoline was added drop wise with stirring till a clear blue coloured solution was obtained. When this blue solution was allowed to evaporate slowly at room temperature, blue shiny crystal appeared after a few days, which were separated from the mother liquor and dried in air. Complex **1** is soluble in methanol, insoluble in water and decomposes at 157 °C. FT-IR (neat) (ν_{max}, cm^{-1}): 3207(w), 3023(w), 2921(w), 1582(s), 1554(s), 1515(m), 1458(m), 1419(m), 1361(s), 1194(m),

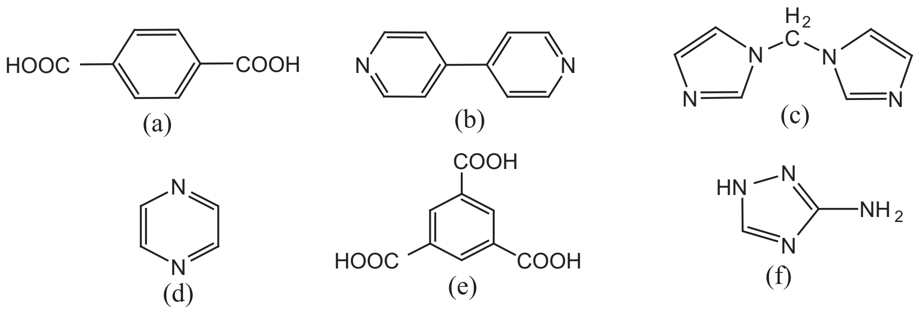

Chart 1. Structural formulae of few organic linkers: (a) terephthalic acid, (b) bipyridine, (c) bis-imidazolyl, (d) pyrazine, (e) 1,3,5-benzenetricarboxylic acid, (f) H-triazole.