Synthesis and structural evaluation of five coordination complexes of benzenepentacarboxylic acid with aza-donor ligands

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ABSTRACT

Synthesis and structural features of five new coordination assemblies, $[Co(\textbf{\textit{bpy}}H)(H_2O)_5](\textbf{BPCH})\cdot(\textbf{\textit{b}-py}\textbf{H}_2)_{0.5}\cdot(H_2O)$ (**1a**), $[\{Cu(H_2O)_3\}\cdot\{Cu_{0.5}(\textbf{\textit{bpy}})_{0.5}(H_2O)_{0.5}\}_2(\mu\text{-}\textbf{BPCH})]$ (**1b**), $[\{Cd_{0.5}(\textbf{BPCH})\}_2\cdot\{Cd_{0.5}(\textbf{\textit{bpy}})(H_2O)_2\}_2]\cdot6(H_2O)$ (**1c**), $[Cu(\textbf{BPCH}_2)(\textbf{\textit{bpyea}}H)]\cdot2(H_2O)$ (**1d**) and $[Cd_2(\textbf{\textit{bpyea}})_{0.5}(oxalate)_{0.5}(\mu\text{-}\textbf{BPC})(H_2O)]\cdot(\textbf{\textit{bpyea}}H_2)\cdot2(H_2O)$ (**1e**), have been reported. All the assemblies were prepared by co-crystallization of benzenepentacarboxylic acid (**BPCH₅**) either with 4,4′-bipyridine (**bpy**) or 1,2-bis(4-pyridyl)ethane (**bpyea**) in the presence of a transition metal ion (either Co(II), Cu(II) or Cd(II)) as the case may be. All the five compounds were synthesized by hydrothermal method and structures were determined by single crystal X-ray diffraction. All the obtained compounds, **1a–1e**, exhibit distinct 3-D polymeric architectures either in the form of stacked layers or host-guest networks in which water molecules play a pivotal role providing additional stabilization by coordinate bonds as well as hydrogen bonds. Other non-covalent interactions such as C—H ⋯ π and π ⋯ π stacking also participate in the formation of exotic 3-D structures of these complexes.

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1. Introduction

In recent times, coordination polymers have been studied extensively with a special attention being paid to metal-organic frameworks (MOF) considering metal ions as nodes and organic ligands as linkers [1]. The notable features of such complexes are the ability to produce materials of aesthetic architectures with tailored physico-chemical properties. Very often these types of molecular materials lead to the construction of supramolecular assemblies through non-covalent interactions such as hydrogen bonds, which play a significant role in formation of extended structures in 1-D, 2-D and 3-D [2]. Synthesis of coordination polymers [3–5] have attracted much attention not only due to their intriguing structural topologies and novel properties for potential applications, but also for bridging different branches of science, particularly chemistry and physics. Thus, applications of these materials are multidimensional, for example, magnetism (long-range ordering and spin cross over), porosity (gas storage and ion and guest exchange), non-linear optical activity, formation of several chiral and reactive networks, heterogeneous catalysis, luminescence etc [6–8].

Among the organic ligands, the ligands with carboxylate functionality expand the horizon of formation of numerous extended framework structures due to their ability to form wide range of possible bridging modes (Scheme 1), as well documented in the literature [9–18].

In this direction, aromatic carboxylates with substitution at 1,2,3-, 1,3,5-, and 1,2,4,5-positions have been studied extensively [11–15]. In fact, polycarboxylic acids possess several interesting characteristics for their ability to create myriad of exotic supramolecular assemblies as specified herein: (a) availability of carboxylic groups both in protonated or deprotonated form (partial or total) and subsequent coordination to the metal ions; (b) ability to form coordination bonds in addition to hydrogen bonds depending upon the degree of deprotonation; (c) conformational flexibility of the carboxylic groups and connectivity to the metal ions in different directions. Based on this understanding, recently, we reported some molecular complexes of 1,2,3,4,5-benzenepentacarboxylic acid (**BPCH₅**) and 4,4'-bipyridine (**bpy**), in which the obtained supramolecular assemblies were rationalized depending on the stoichiometric ratio of the components [2a]. However, to our
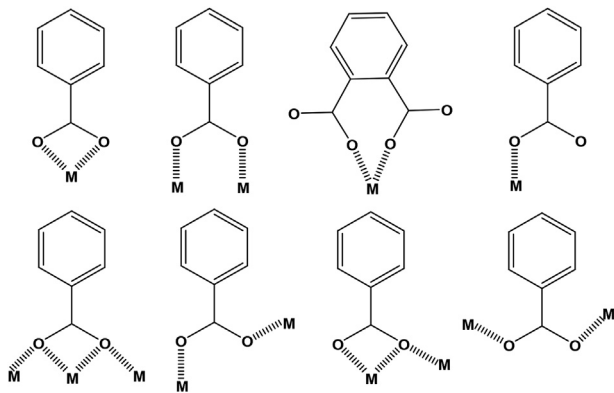
Scheme 1. Different coordination modes of aromatic carboxylic acid to metal.

knowledge, **BPCH₅** has not been well explored in the areas of co-ordination polymers, except for a few reports [16–18] appeared in the recent literature. For instance, Zang and co-workers [18] have reported a coordination polymer of **BPCH₅** highlighting the met-allophilic attraction in coinage metals like Ag(I) where a three dimensional framework with a honeycomb like structure has been produced.

Since **BPCH₅** can yield open-frame structures in conjunction with metal ions same as other polycarboxylic acids studied so far, we programmed further to prepare coordination polymers of **BPCH₅**. We report herein the synthesis and characterization by single-crystal X-ray diffraction and structural features of five complexes formed by Co(II), Cu(II) and Cd(II) with **BPCH₅**, in pres-ence of spacer ligands like 4,4'-bipyridine (**bpy**) and 1,2-*bis*(4-pyridyl)ethane (**bpyea**), as shown in Scheme 2.

2. Experimental section

2.1. Materials

All chemicals, **BPCH₅**, **bpy**, **bpyea**, metal salts (Cu(NO₃)₂·3H₂O, Co(NO₃)₂·6H₂O and Cd(CH₃COO)₂·H₂O) are of analytical grade and purchased from commercial suppliers and used as such without any further purification. Water used was from a Milli-Q ultrapure water purification system.

2.2. Preparation of the complexes

The complexes were prepared by hydrothermal method by carrying out reactions in a 50 mL Teflon-lined autoclave at a neutral pH. In a typical example, complex **1a** was prepared by placing a mixture of Co(NO₃)₂·6H₂O (29.1 mg, 0.1 mmol), **BPCH₅** (29.8 mg, 0.1 mmol) and **bpy** (15.6 mg, 0.1 mmol) that was kept in a Teflon flask with about 15 mL of water in an autoclave and heated at

140 °C for 4 days. The resultant neutral solution was allowed for slow evaporation over a period of 10 day at ambient conditions. The obtained crystalline compound was collected by filtration, washed with water and dried in air. The washed compounds contained diffraction quality block shaped single crystals.
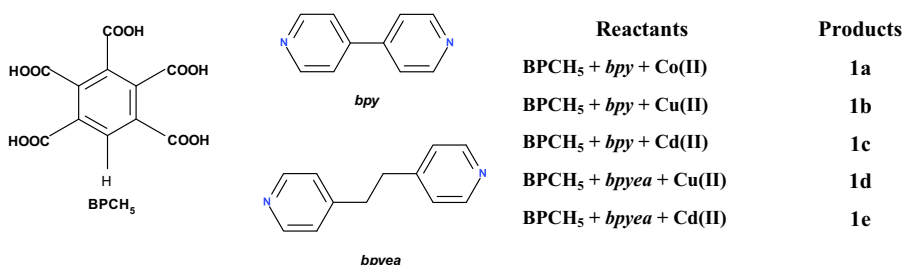
2.3. X-ray crystallography of **1a**–**1e**

Single crystals of **1a**–**1e** were carefully chosen after viewing through a Leica microscope supported by a rotatable polarizing stage and CCD camera. The crystals were glued to a thin glass fiber using an adhesive (acrylate cyano) and mounted on a diffractom-eter equipped with APEX CCD area detector using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The X-ray in-tensity data were collected with varying exposure time, depending upon the quality of the crystal(s). The data collection was quite smooth in all the cases. The intensity data were processed using Bruker's suite of data processing programs (SAINT) [19] and ab-sorption corrections were applied using SADABS [20]. The structure solution of all the complexes has been carried out by the direct methods and refinements were performed by full matrix least squares on F^2 using the SHELXTL-PLUS [21] suite of programs. All the non-hydrogen atoms were refined anisotropically, while the hydrogen atoms, either located or fixed, were refined isotropically. However, in some structures, water molecules are reported without hydrogen atoms as appropriate positions could not be determined by all possible means.

In all the cases refinements were smooth and the final re-finements converged at R_1 ($I > 2\sigma(I)$) values of 0.0412, 0.0788, 0.0702, 0.0588 and 0.0432 for **1a**–**1e** respectively. Crystal data and details of X-ray intensity data collection for **1a**–**1e** are listed in Table 1. The intermolecular interactions were computed using PLATON [22]. All the structural packing diagrams are generated using Diamond software [23]. The details of coordination envi-ronment of the metal centers with distances and angles are given in Table 2. The characteristics of hydrogen bonds are compiled in Table 3.

2.4. Thermogravemetric analysis

Thermogravimetric analyses were carried out on a Mettler Toledo TGA/SDTA 851e module, wherein a typical experimental sample (4–7 mg) was placed in an alumina sample pan and heated in the temperature range 30–500 °C under a continuously purged dry air atmosphere (flow rate 50 mL/min) at a heating rate of 10 °C/min. The respective TGA plots have been given in Fig. S1 in Sup-porting Information File.

Reactants	Products
BPCH₅ + *bpy* + Co(II)	**1a**
BPCH₅ + *bpy* + Cu(II)	**1b**
BPCH₅ + *bpy* + Cd(II)	**1c**
BPCH₅ + *bpyea* + Cu(II)	**1d**
BPCH₅ + *bpyea* + Cd(II)	**1e**

Scheme 2. Chemical structures of the ligands and the outlined schemes of the reactions.