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Syntheses, structures and magnetic properties of Co(II) complexes based on H_4BTEC and 2-(*n*-pyridyl)benzimidazole ($n = 2$, 3, and 4)

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Abstract

The hydrothermal reactions of cobalt(II) salts with 1,2,4,5-benzenetetracarboxylic acid (H_4BTEC) and 2-(*n*-pyridyl)benzimidazole ($n = 2$, 3, 4) led to the formation of three new coordination complexes, Namely, $[Co(BTEC)_{0.5}(2\text{-PyBIm}) \cdot H_2O] \cdot H_2O$ (**1**), $[Co(BTEC)_{0.5}(3\text{-PyBIm}) \cdot H_2O]$ (**2**), $[Co(H_2BTEC)(4\text{-PyBIm})_2] \cdot H_2O$ (**3**) were studied. The H_4BTEC ligands adopt different coordination modes according to the orientation of the pyridyl-sustituted benzimidazole. In complex **1**, the $BTEC^{4-}$ acts as four-dentate bridging ligand with all carboxylate groups adopt unidentate coordination fashion, leading a two-dimensional coordination network. While in **2**, two of the four carboxylate groups adopt chelating bi-dentate coordination mode, and the others demonstrate uni-dentate coordination fashion; leading a one-dimensional chain with the nearest Co ··· Co separation being 5.057 Å. In **3**, the adjacent carboxylate groups chelate the cobalt(II) atom in the uni-dentate coordination fashion, leading a one-dimensional undulating chain. Finally, all the complexes are extended into three-dimensional framework via hydrogen-bonding as well as π–π interactions. The thermal stabilities and temperature-dependent magnetic susceptibilities for the three complexes were also studied.

Keywords: Benzimidazole; Supramolecular; Benzoate; Crystal structure; Self-organization; Hybrid material; Hydrogen-bonding; Coordination complex

1. Introduction

The rational design and construction of coordination polymers based upon assembly of metal ions and multifunctional organic ligands is an increasingly research field on account of their intriguing structural topologies and potential applications as functional materials [1]. In this field, the aromatic polycarboxylate transition metal complexes has received considerable attention owning to the variety of bridging abilities of polycarboxylate in the formation of porous frameworks [2]. The 1,2,4,5-benzenetetracarboxylic acid (H_4BTEC) is a good choice for the construction of polymeric structures for the abundant carboxylic groups, which can act not only as hydrogen-bond acceptor but also donor, adopt versatile coordination mode as well as multiplicity deprotonation under certain circumstance [3]. The complexes based on H_4BTEC and other ligands demonstrate that the finally structure is greatly affected by the auxiliary ligands [4], and much work is still required to extend the knowledge of relevant structural types and establish proper synthetic strategies which could control dimensionality of the complexes and leading the desired organic–inorganic frameworks.

Herein, we report the syntheses and structural characterizations of three new cobalt(II) complexes based on H_4BTEC and 2-(*n*-pyridyl)benzimidazole ligand ($n = 2$, 3, and 4). The results show the orientation of the 2-(*n*-pyridyl)benzimidazole do great effects on the coordination fashion of H_4BTEC ligand, thus leading great difference on the complexes structures. Furthermore, the hydrogen

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bonds (between noncoordinating N–H (or N) groups and other acceptors) as well as π–π interactions (between the aromatic rings of the ligands) play an important role in the final supramolecular architectures of the complexes.

2. Experiment

2.1. General

The ligands 2-(*n*-pyridyl)benzimidazole ($n = 2$, 3, and 4) were synthesized according to the procedure reported by Fieselman [5]. Other reagents and solvents employed were commercially available and used as received without further purification. Elemental analyses were carried out on an EA1110 CHNS-0 CE element analyzer and the IR spectra (KBr pellets) were recorded at a Nicolet Magna 750 FT-IR spectrometer in the range of 400–4000 cm^{-1}. Thermogravimetric analyses (TGA) were performed with a Netzsch STA-499 C thermoanalyzer under air atmosphere (30–800 °C range) at a heating rate of 10 °C/min. Variable temperature magnetic susceptibilities were measured on a model CF-1 superconducting extracting sample magnetometer; the powdered sample were kept in the capsule for weighing.

2.2. Syntheses

2.2.1. Synthesis of [Co (2-PyBIm)(BTEC)$_{0.5}$ · H_2O] · H_2O (1)

A solution of $CoCl_2 \cdot 4H_2O$ (0.249 g, 1.05 mmol), 2-PyBIm (0.195 g, 1.0 mmol), H_4BTEC acid (0.12 g, 0.50 mmol), NaOH (0.064 g, 1.6 mmol) and H_2O (15 mL) was stirred under ambient conditions, then sealed in a Teflon-lined steel autoclave, heated at 160 °C for 5 days, and cooled to room temperature. The resulting product was recovered by filtration, washed with distilled water and dried in air. (80% yield) Anal. Calcd for $C_{17}H_{14}CoN_3O_6$: C, 49.15; H, 3.40; N, 10.12. Found: C, 48.81; H, 3.62; N, 9.95. IR (KBr pellet, cm^{-1}): 3436.3s, 1581.7m, 1490.2w, 1455.6w, 1445.5w, 1376.4s, 1322.1w, 1234.3w, 1158.8m, 1139.1w, 1051.5w, 1005.0w, 985.8m, 922.3w, 866.9w, 816.6m, 749.1s, 696.2m, 605.2m.

2.2.2. Synthesis of [Co(3-PyBIm)(BTEC)$_{0.5}$ · H_2O] (2)

Similar to the preparation of **1**, the hydrothermal reaction of a solution consisted of $CoCl_2 \cdot 4H_2O$ (0.249 g, 1.05 mmol), 3-PyBIm (0.195 g, 1.0 mmol), H_4BTEC acid (0.12 g, 0.50 mmol), NaOH (0.064 g, 1.6 mmol) and H_2O (15 mL). (65% yield) Anal. Calcd for $C_{17}H_{12}CoN_3O_5$: C, 51.40; H, 3.04; N, 10.58. Found: C, 51.66; H, 3.55; N, 10.38. IR (KBr pellet, cm^{-1}): 3160.8s, 1586.4s, 1488.8m, 1442.8m, 1382.2s, 1318.8m, 1288.9m, 1232.1w, 1197.6w, 1138.8m, 1058.9m, 1031.0w, 1005.3w, 973.3s, 873.6s, 831.2m, 817.2m, 754.6s, 694.0s, 678.3m, 601.5s, 498.5s.

2.2.3. Synthesis of [Co(4-PyBIm)$_2$(H_2BTEC)] · H_2O (3)

A solution of $Co(CH_3COO)_2 \cdot 4H_2O$ (0.136 g, 0.55 mmol), 4-PyBIm (0.195 g, 1.0 mmol), H_4BTEC acid (0.12 g, 0.50 mmol), and H_2O (15 mL) was stirred under ambient conditions, then sealed in a Teflon-lined steel autoclave, heated at 160 °C for 5 days, and cooled to room temperature. The resulting product was recovered by filtration, washed with distilled water and dried in air. (83% yield) Anal. Calcd for $C_{34}H_{24}CoN_6O_9$: C, 56.76; H, 3.36; N, 11.68. Found: C, 56.81; H, 3.62; N, 11.95. IR (KBr pellet, cm^{-1}): 3398.2s, 1615.9s, 1573.7s, 1498.4w, 1447.1w, 1374.9s, 1316.8m, 1287.0w, 1237.4m, 1018.0w, 972.0w, 834.6w, 745.0s, 698.9m.

2.3. X-ray crystallography

Suitable single crystals of complexes **1**–**3** were carefully selected under an optical microscope and glued to thin glass fibers. The diffraction data were collected on a Siemens Smart CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. An empirical absorption correction was applied using the SADABS program [6]. The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 by using the SHELXTL-97 program package [7]. No attempts were made to locate the hydrogen atoms of water in complex **3**; the other hydrogen atoms were generated geometrically. The crystallography details for the structures determination of complexes **1**–**3** are presented in Table 1. Selected bond lengths and bond angles are listed in Table 2. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC reference number 601997–601999 for complexes **1**–**3**. Copies of information may be obtained from The Director, CCDC, 12 union road, CB2 1EZ, UK (Fax: +44 1233 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

3. Result and discussion

Attempts to get crystals suitable for X-ray diffraction from the reaction of metal salt, $BTEC^{4-}$ (or H_2BTEC^{4-}) and PyBIm in solution conditions failed. Insoluble precipitates were obtained owing to rapid polymerization. Complete deprotonation of H_4BTEC occurred in complexes **1** and **2**, try to obtain the product with partially deprotonated H_4BTEC failed; replace of $CoCl_2 \cdot 4H_2O$ and NaOH with pertinent $Co(CH_3COO)_2 \cdot 4H_2O$ resulting in the products different from **1** and **2** but not suitable for X-ray diffraction. In **3**, the H_4BTEC is partially deprotonated. When the pH of the reaction system was adjusted to higher conditions, other products produced. These relevant works are still under investigation in our laboratory.

The TGA diagrams show these complexes **1**–**3** have similar stabilities and behaviors in the range of 100–500 °C, all displaying loss of water molecule around 80 °C to 220 °C. Complex **1** exhibits loss of the lattice as well as coordination water molecule between the range of 175 and 222 °C (4.53% weight loss observed; 4.34% calculated), the complexes does not show weight loss in the range of 222–