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Synthesis, characterizations and catalytic studies of a new two-dimensional metal – organic framework based on Co–carboxylate secondary building units

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ABSTRACT

A metal–organic framework $[Co_3(BDC)_3(DMF)_2(H_2O)_2]$ was synthesized and structurally characterized. X-ray single crystal analysis revealed that the framework contains a 2D polymeric chain through coordination of 1,4-benzenedicarboxylic acid linker ligand to cobalt centers. The polymer crystallize in monoclinic $P2_1/n$ space group with $a=13.989(3)$ Å, $b=9.6728(17)$ Å, $c=16.707(3)$ Å, and $Z=2$. The polymer features a framework based on the perfect octahedral Co–O6 secondary building units. The catalytic activities of $[Co_3(BDC)_3(DMF)_2(H_2O)_2]_n$ for olefins oxidation was conducted. The heterogeneous catalyst could be facilely separated from the reaction mixture, and reused three times without significant degradation in catalytic activity. Furthermore, no contribution from homogeneous catalysis of active species leaching into reaction solution was detected.

1. Introduction

Metal–organic frameworks (MOFs) have received a great deal of interest and represented an active area of coordination chemistry not only by their multiple potential applications in gas storage, separation, magnet, optoelectronics and catalysis, but also by their enormous variety of intriguing structural topologies [1–5]. The most powerful strategy for the architecture of diverse structural topologies in MOFs as coordination polymers is the selection of appropriate multidentate ligand as a linker in connecting metal ions to achieve one-, two-, or three-dimensional crystalline network structures [6–9]. Thus, there has been considerable amount of research on multicarboxylate ligands to design metal-containing polymers [10–13].

Among transition metal in MOFs, there has been a great attention in coordination chemistry of cobalt complexes with carboxylate ligands, due to the fact that polynuclear cobalt carboxylates are suitable candidates for structural assembly of new coordination solids with interesting network architectures [14–16]. As multicarboxylate ligand, 1,4-benzenedicarboxylic acid (H_2BDC) with its derivetives and 1,3,5-benzenetriacetic acid have been used in the synthetic systems because they can exhibit a short bridge via one carboxylic group or a long one via the benzene ring which leads to varieties of multi-dimensional MOFs with different kinds of topologies [17–19].

To enrich this field of research, we used H_2BDC as the rigid multicarboxylate ligand to synthesize new cobalt MOF. The rigid aromatic unit in H_2BDC ligand as spacer seemed to be promising to control and adjust stable framework. Here, we report hydrothermal synthesis, characterizations and catalytic studies of MOF of $[Co_3(BDC)_3(DMF)_2(H_2O)_2]$ formed between Co-centers and H_2BDC ligands. Particular attention is focused on the catalytic efficiency of the MOF in olefin oxidation reaction.

2. Experimental section

2.1. Materials and instruments

All reagents for synthesis and analysis were obtained commercially with analytical grade and used without further purification. The elemental analysis (CHN) of compound was obtained from a Carlo ERBA Model EA 1108 analyzer. Fourier transform infrared (FT-IR) spectrum was obtained by utilizing a Unicam Matson 1000 FT-IR spectrophotometer using KBr disks at room temperature. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer TGA7 analyzer in N_2 atmosphere with a heating rate of 5 °C min^{-1}. Powder X-ray diffraction (XRD) patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu*Kα* radiation. Inductively coupled plasma (ICP) was performed by ICP–MS HP 4500. The products of olefins oxidation reaction were determined and

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analyzed by a HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column (phenylmethylsiloxane 30 m × 320 μm × 0.25 μm) and a flame-ionization detector.

2.2. Synthesis of $[Co_3(BDC)_3(DMF)_2(H_2O)_2]_n$

A DMF solution (5 mL) of $CoCl_2 \cdot 6H_2O$ (291 mg, 1 mmol) was added to a solution of 1,4-benzenedicarboxylic acid (H_2BDC) (166 mg, 1 mmol) in 5 mL DMF in the small sample vessel. The solution was heated for 48 h at 80 °C without any stirring or shaking and then the temperature was gradually decreased to 60 °C (2 $^\circ C\,h^{-1}$). After 2 days that solution was kept in 60 °C, purple crystals of $[Co_3(BDC)_3(DMF)_2(H_2O)_2]_n$ (85% yield based on H_2BDC) were obtained. The crystals were washed with DMF (3 mL, two times) and dried in air to yield pure product. Anal. Cal: for $C_{30}H_{24}Co_3N_2O_{16}$: C, 42.42; H, 3.32; N, 3.30. Found: C, 42.63; H, 2.86; N, 3.28. FT-IR (KBr 4000–400 cm^{-1}): 3491 (br), 2931 (w), 1663 (s), 1619 (s), 1559 (s), 1418 (s), 1254 (w), 1115 (m), 855 (m), 813 (m), 760 (s), 693 (s), 655 (m), 468 (m).

2.3. X-ray crystallographic studies

Single crystal of the complex was mounted in a random orientation on a glass fiber. Data collection was carried out at 296 K on an Oxford Diffraction X calibur four-circle kappa geometry single-crystal diffractometer with a Sapphire 3 CCD detector, using a graphite monochromated Mo*K*α ($\lambda = 0.71073$ Å) radiation, and applying the CrysAlis Software system. The crystal–detector distance was 50 mm. Data reduction, including absorption correction, was done by the CrysAlice RED program. The structure was solved by direct methods implemented in the SHELXS-97 program [20]. The coordinates and the anisotropic displacement parameters for all non-hydrogen atoms were refined by full-matrix least-squares methods based on F^2 values using the SHELXL-97 program. All hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent C atoms with C–H = 0.93 and 0.96 Å for CH and CH_3, respectively, and with $U_{iso}\,(H) = k \times U_{eq}$ (C), where $k = 1.2$ for CH H atoms and $k = 1.5$ for CH_3 H atoms [21]. Graphical work was performed via OLEX2 [22]. The termal ellipsoids were drawn at the 50% probability level.

2.4. General process for catalytic oxidation reaction

For the heterogeneous olefins oxidation, the reactions was done in a two-necked round-bottom flask fitted with a condenser and placed in a temperature controlled oil bath. Typically, 1 mmol of the substrate was taken in 2 mL solvent, followed by the addition of 3 mg catalyst (0.01 mmol to Co center) and then, the mixture was heated at 75 °C under stirring. The reaction began with the addition of *tert*-butyl hydroperoxide (TBHP) (equimolar with respect to substrate). The products from the reaction mixture were analyzed by Gas Chromatography in the presence of chlorobenzene as an internal standard and were identified through being compared with known standards.

2.5. General procedure for recyclability of $[Co_3(BDC)_3(DMF)_2(H_2O)_2]_n$ catalysts

The recyclability of the $[Co_3(BDC)_3(DMF)_2(H_2O)_2]_n$ catalyst was investigated in oxidation reaction of styrene in the presence of TBHP in 1,2-dichloroethan at 75 °C for 7 h. Then, after the first catalytic reaction, the solid catalyst was easily isolated by centrifuge and recovered by being washed with solvent and dried at 70 °C. Afterwards, catalyst was used for the next run under the same reaction condition as the first run.

3. Result and discussion

3.1. Crystal structure description

Single-crystal X-ray structure analysis revealed that $[Co_3(BDC)_3(DMF)_2(H_2O)_2]_n$ crystallizes in the monoclinic $P2_1/n$ space group (Fig. 1). The MOF structure is composed of Co–O_6 octahedral linked by 1,4-benzenedicarboxylate linkers (Fig. 2). The structure of $[Co_3(BDC)_3(DMF)_2(H_2O)_2]$ coordination polymer is a 2D-periodic framework made of discrete secondary building units (SBUs) each of which is constructed from $Co^{II}O_6$ corner shared octahedral (Fig. 3). The crystal data is shown in Table 1. The Co–carboxylate 2D coordination polymer of $[Co_3(BDC)_3(DMF)_2(H_2O)_2]$ is formed by two-dimensional infinite straightforward chains through covalent interactions (Fig. 4). The MOF structure is composed of Co–O–C units in which the carboxylate links are coordinated to the metal centers in at least one of the following modes as shown in Fig. 5 that helps to form a 2D-polymeric chain.

There are two distinct symmetrically independent Co centers in the crystal structure which are further mutually linked by benzene units from 1,4-benzendicarboxylate links furnishing 2D framework in the (1 0 1) plane. The Co(II) ions located in general positions, Co1 and Co2, are surrounded by six oxygens in the octahedral

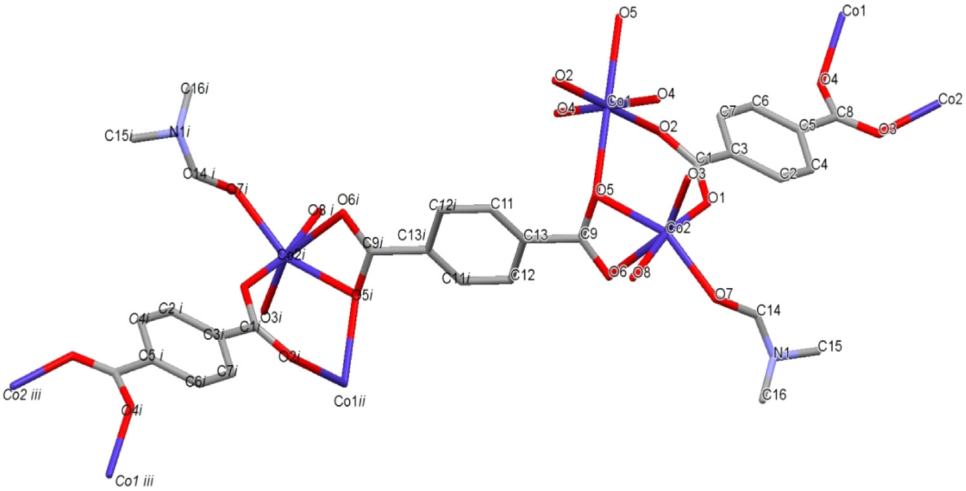

Fig. 1. Coordination environment of Co(II) in $[Co_3(BDC)_3(DMF)_2(H_2O)_2]_n$. The hydrogen atoms are omitted for clarity. (*i*) $1-x,\ -y,\ -z$; (*ii*) $x,\ -1+y,\ z$; (iii) $1/2-x,\ -1.5+y,\ -1/2-z$.