Ionothermal synthesis and structural transformation targeted by ion exchange in metal-1,3,5-benzenetricarboxylate compounds

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ABSTRACT

Ionothermal reactions of 1,3,5-benzenetricarboxylate acid (H3BTC) and Ni(NO3)2, Co(NO3)2 and Cu(NO3)2 gave two discrete 32-membered ring-like allomers, [M2(HBTC)(NH2CONH2)2(H2O)4]·3H2O (M=Ni(1), Co(2)) and one layered [Cu2(BTC)Cl(H2O)] (3). The weak interactions in 1 can be deconstructed to some degree in ion exchange by exploring the factors of divalent and trivalent metal species, metal concentration and soaking time, which are demonstrated by PXRD and N2 absorption. Cu2+ has the highest N2 adsorbance when soaking with 1, and 1 can keep structure stable when Cu2+ below 0.16 mol L−1 and the soaking time within 24d. As Cu2+ beyond 0.16 mol L−1 and the soaking time beyond 24d, the structure of compound 1 starts to transform with the crystal morphology from clear pale green to opaque blue. Ionothermal reactions of compound 1 with different Cu2+ amounts obtained Ni2+-Cu2+ hetero complexes, whose PXRD patterns are similar to that of 3 and EDS indicates Cu2+% increases with Cu2+ additions and close to 100% as Cu2+ being 1.6 mmol. It suggests that 3 is a controlled product and Cu2+ can transform discrete compound 1 into 2D compound 3.

1. Introduction

Ionothermal synthesis as an environment-friendly method has received remarkable attention in the latest decade [1–3], in which ionic liquids (ILs) behave as reaction media, structural templates or charge-compensating groups [4,5]. ILs mainly divide into two types of imidazolium-based ILs and deep eutectic solutions (DESs), possessing common distinguishing features: high ionic conductivity, non-flammability, negligible vapor pressure, and so forth [6,7], which contributes much for new-type materials with intriguing structures, such as zeolite, zeo-type meso- and macroporous materials, and metal-organic framework (MOF) materials [8,9]. Different from hydrothermal or other new emerging synthetical methods (such as surfactant-thermal method [10]), ILs are reasonably expected to offer significantly different reaction environments to produce new-type MOF materials. Enormous effort has been devoted to the applied ionothermal synthesis of novel MOF materials [11–13], especially with 1,3,5-benzenetricarboxylate acid as organic spacer [14]. Our previous work major focus on imidazolium-based ionic liquids as reaction media in the metal-benzene polycarboxylate systems, showing the effect of metal-direction, cationic template, anionic groups on the MOFs’ structures and properties [15]. In the metal-benzene polycarboxylate systems, the cavities of the frameworks are often occupied by the 1-methyl-3-alkyl-imidazolium templates, thus to limit some applications, such as gas adsorption, catalyst. Compared to imidazolium-based ILs, the components in DESs can be the auxiliary ligands besides reaction media, thus to make it possible to obtain MOFs with available cavities. It suggests DESs may have better applications in MOF materials [16].

Herein, we chose a DES composed of choline chloride and urea with a certain ratio as IL media in the synthetical process. We fixed 1,3,5-benzenetricarboxylate acid as ligand, and three salts of Ni(NO3)2, Co(NO3)2 and Cu(NO3)2 as metal sources to obtain two discrete 32-membered ring-like allomers, [M2(HBTC)(NH2CONH2)2(H2O)4]·3H2O (M=Ni(1), Co(2)) and one 2D layered [Cu2(BTC)Cl(H2O)] (3). These compounds were characterized by single crystal X-ray diffraction, powder X-ray diffraction (PXRD), FT-IR, N2 adsorption, inductively coupled plasma (ICP), energy dispersive X-ray spectrum (EDS). The weak interactions can be deconstructed when soaked with metal cations solutions. Compound 1 also shows a structural transformation into compound 3 with the addition of Cu2+.
2. Experimental

2.1. Materials and physical measurements

The reagents and solvents were used directly as supplied commercially without further purification. FT-IR spectra were collected from KBr pellets (Aldrich, > 99%, FT-IR grade) with a Bruker Tensor 27 FT-IR spectrometer in the range of 4000–400 cm⁻¹. PXRD data for the materials were collected at ambient temperature with a Rigaku D-Max−3c (Japan) diffractometer (Cu-Kα₂ X-radiation, λ₁=1.540598 Å and λ₂=1.544426 Å), equipped with an X’Celerator detector and a flatplate sample holder in a Bragg-Brentano para-focusing optics configuration (40 kV, 50 mA). Intensity data were collected in the 5°≤2θ≤60° range by the step counting method (the step being 0.02°) in continuous mode. Specific surface area and pore structure parameters of compound 1 were obtained by measuring N₂ adsorption isotherms under a relative pressure of 10⁻⁶–1 MPa at 77 K on a Micromeritics ASAP2020 HD88 specific area and porosity analysis meter. The Ni²⁺ and Cu²⁺ concentrations in the Cu(NO₃)₂ ethanol solutions soaking with compound 1 were determined on a Bruker M90 ICP mass spectrometer. The Ni²⁺ and Cu²⁺ contents in the hetero complexes were determined by EDS tests on a Quanta 200 environmental scanning electron microscope.

2.2. Synthesis of the compounds

2.2.1. Synthesis of [Ni₂(HBTC)₂(NH₂CONH₂)₂(H₂O)₄]·3H₂O (1)

0.20 mmol, 0.058 g Ni(NO₃)₂·6H₂O and 0.20 mmol, 0.0422 g H₃BTC were placed in a crystallisation vial placed in a Rigaku Mercury CDiff diffractometer equipped with a graphite-monochromated Mo-Kα radiation (λ=0.71073 Å) at 293(2) K. The intensity data were collected by the ω scan technique and were reduced using CrystalClear program [19]. The crystal structures of compounds 1–3 were solved by direct method using SHELX[20] package of crystallographic software [20], corrected for absorption by the multiscan semiempirical method implemented in SADABS [21], and refined by full-matrix least-squares technique on F². All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at geometrically calculated positions to refine with isotropic thermal parameters included in the final stage of the refinement. A summary of the structural determination and refinement for 1–3 is listed in Table 1. The selected bond distance and angles are listed in Supporting information (Table S1).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center (the deposition numbers CCDC 1510315–1510317 for 1–3 respectively). These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

2.2.2. Synthesis of [Co₂(HBTC)₃(NH₂CONH₂)₃(H₂O)₄]·3H₂O (2)

Prepared as described in 1, compound 2 was obtained from the mixture of 0.20 mmol, 0.0486 g Cu(NO₃)₂·3H₂O, and 0.20 mmol, 0.0418 g H₂BTC mixed with 1 mmol, 0.1395 g choline chloride and 2 mmol, 0.120 g urea. The mixture was kept inside the furnace at 100 °C for 3 days, and then naturally cooled to ambient temperature, then added with Cu(NO₃)₂ of 0.007, 0.013, 0.025, 0.050, 0.100, 0.150, 0.200, 0.400, 0.800, 1.000, 1.200, 1.300, 1.400, 1.500, and 1.600 mmol respectively to react at 100 °C for 3 days, and naturally cooled to ambient temperature to give blue prism crystals.

2.2.3. Synthesis of [Cu₂(BTC)₃C(CH₂)₃]·(H₂O)₁·3H₂O (3)

Prepared as described in 1, compound 3 was obtained from the mixture of 0.20 mmol, 0.0486 g Cu(NO₃)₂·3H₂O, and 0.20 mmol, 0.0418 g H₂BTC mixed with 1 mmol, 0.1395 g choline chloride and 2 mmol, 0.120 g urea to obtain the red crystals. FT-IR data (in KBr, cm⁻¹) for 1: 3402(m), 3319(m), 3201(m), 1654(m), 1612(s), 1550(s), 1429(s), 1367(s), 1261(m), 1155(w), 1101(w), 1022(w), 927(w), 763(m), 717(m), 609(m), 541(m). These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

3. Results and discussion

3.1. Crystal structures of compounds 1–3

Compounds 1 and 2, [M₂(HBTC)₃(NH₂CONH₂)₃(H₂O)₄]·3H₂O (M=Ni(I) and Co (2)) are allomers with the same structural details, such as same coordination spheres of M(II) centers and the coordination fashions of BTC⁻ ligands. Therefore, only compound 1 will be discussed, the structural motif of compound 2 is listed in Supporting information (Fig. S1).

The asymmetric unit of compound 1 consists of one Ni(II) center, one BTC⁻⁻⁻ ligands, one urea, two coordinated water and one and half lattice water. The six-coordinated Ni(II) center locates in a distorted octahedron geometry. Two water molecules and one urea as terminal ligands link to Ni(II) center into a [Ni(H₂O)₉(NH₂CONH₂)₃] SBU. Four [Ni(H₂O)₉(NH₂CONH₂)₃] SBUs are interconnected alternately by two kinds of μ₃-HBTC⁻⁻⁻ ligands with the coordination modes of bis-chelating and bis-monodentate (Scheme 1a-b) into a 32-membered ring (Fig. 1). The weak interaction system in compound 1 shapes around amino groups (Supporting information, Table S2). Through the
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