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Synthesis, structure and sorption property of metal complexes with mixed multicarboxylate and imidazole-containing ligands

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Zinc(II) and nickel(II) frameworks $[Zn_2(L)(BTC)(NO_3)]\cdot H_2O\cdot 2CH_3CN$ (**1**), $[Ni_2(L)(H_2O)_3(HBTC)_2]\cdot 3.6H_2O$ (**2**), $[Ni(L)(H_2O)_2](BPDC)\cdot 2H_2O$ (**3**), $[Ni(L)(H_2O)(BPDC)]\cdot 4H_2O$ (**4**) and $[Ni_2(L)(MeOH)_4(BPDC)_2]\cdot 2H_2O$ (**5**) were synthesized by reactions of corresponding metal salts with 3,3′,5,5′-tetra(1H-imidazol-1-yl)-1,1′-biphenyl (L) and multicarboxylic acids of 1,3,5-benzenetricarboxylic acid (H_3BTC), 4,4′-biphenyldicarboxylic acid (H_2BPDC). Complex **1** is a 2-fold interpenetrating 3D net, while **2** is a 2D network with infinite 1D hinged Ni(II)-L chains linked by $HBTC^{2-}$ ligands. **3**, **4** and **5** were obtained by using different molar ratios of L, H_2BPDC and Ni(II) salt, and found to show different 2D network structures in which the numbers of coordinated carboxylate groups of $BPDC^{2-}$ are 0, 1 and 2, respectively. Sorption properties of **1**–**5** were investigated.

1. Introduction

During the past decades, the study of metal-organic frameworks (MOFs) has received considerable attention not only because of their fascinating architectures but also due to their interesting properties and potential applications. On the one hand, the assembly process can be influenced by factors such as the predesigned organic linker, the nature of metal ion, metal-to-ligand ratio, and reaction temperature etc [1–9]. Particularly, the organic linkers may have remarkable influence on the assembly process and as a result on the structure and property of MOFs. For example, Zhou and his coworkers focus their attention on tuning the topology and functionality of MOFs through the ligand design [10]. On the other hand, MOFs with varied structures can be obtained by tuning these factors. Recently, the mixed ligand strategy has been utilized in the synthesis of MOFs, especially the mixed multicarboxylate and N-donor ligands were widely used [11,12]. Meanwhile, our group has made efforts on construction of MOFs with imidazole-containing ligands and the results have shown that the imidazole-containing ligands combine with varied metal salts leading to the formation of MOFs with different structures such as individual cages, one- (1D), two- (2D) and three-dimensional (3D) frameworks [13,14]. In addition, multicarboxylic acids such as 1,3,5-benzenetricarboxylic acid (H_3BTC) and 4,4′-biphenyldicarboxylic acid (H_2BPDC) are the most extensively used organic ligands in the construction of MOFs due to their rigid multicarboxylate groups and versatile coordination modes [15–21]. From these studies, it can be seen that the varied coordination modes of the carboxylate groups can enrich the structure, but at the same time, make difficult to predict and control the structure of MOFs. While in the case of MOFs with N-donor linkers such as pyridine, imidazole and/or azole-containing ligands, there must be counter anions since these kind of N-donor ligands are neutral and the metal ions have positive charges. The counter anions occupy the voids and decrease the porosity of the frameworks. Thus the mixed multicarboxylate and N-donor ligands may overcome such disadvantages of the solely ligands, and provide useful approach to construct desired MOFs [12].

In this work, we introduced rigid 3,3′,5,5′-tetra(1H-imidazol-1-yl)-1,1′-biphenyl (L) as imidazole-containing ligand assembling with multicarboxylic acids of H_3BTC and H_2BPDC and corresponding metal salts to give five coordination polymers with different structures, namely $[Zn_2(L)(BTC)(NO_3)]\cdot H_2O\cdot 2CH_3CN$ (**1**),

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$[Ni_2(L)(H_2O)_3(HBTC)_2]\cdot3.6H_2O$ (**2**), $[Ni(L)(H_2O)_2](BPDC)\cdot2H_2O$ (**3**), $[Ni(L)(H_2O)(BPDC)]\cdot4H_2O$ (**4**) and $[Ni_2(L)(MeOH)_4(BPDC)_2]\cdot2H_2O$ (**5**). They were characterized by elemental analysis and X-ray crystallography. The thermal stability and sorption properties of the complexes were investigated.

2. Experimental

2.1. Materials and measurements

All commercially available chemicals and solvents are of reagent grade and were used as received without further purification. The ligand L was prepared according to the reported procedures [22]. Elemental analyses for C, H and N were performed on a Perkin–Elmer 240C Elemental Analyzer at the analysis center of Nanjing University. Thermogravimetric analyses (TGA) were performed on a simultaneous SDT 2960 thermal analyzer under nitrogen with a heating rate of 10 °C min^{-1}. FT-IR spectra were recorded in the range of 400–4000 cm^{-1} on a Bruker Vector22 FT-IR spectrophotometer using KBr pellets. Power X-ray diffraction (PXRD) patterns were obtained on a Shimadzu XRD-6000 X-ray diffractometer with Cu Kα (λ = 1.5418 Å) radiation. Sorption experiments were carried out on a Belsorp-max volumetric gas sorption instrument. The bulk samples of **1**′–**5**′ for sorption experiments were obtained by heating the fresh complexes at 180 °C for **2** and 200 °C for others for 10 h under high vacuum to remove the coordinated and free solvent molecules.

2.2. Preparation of $[Zn_2(L)(BTC)(NO_3)]\cdot H_2O\cdot2CH_3CN$ (*1*)

A mixture of L (10.5 mg, 0.025 mmol), H_3BTC (6.3 mg, 0.03 mmol), $Zn(NO_3)_2\cdot6H_2O$ (14.9 mg, 0.05 mmol), 2 mL CH_3CN and 6 mL H_2O was adjusted to pH ≈ 7 with 0.5 mol L^{-1} NaOH solution. Then the mixture was sealed into a Teflon-lined stainless steel container and heated at 180 °C for 3 days. After being cooled to room temperature, yellow block crystals were obtained in 70% yield based on L. Anal. Calcd for $C_{37}H_{29}N_{11}O_{10}Zn_2$: C, 48.39; H, 3.18; N, 16.78%. Found: C, 48.27; H, 3.12; N, 16.69%. IR (KBr pellet, cm^{-1}): 3416 (m), 3137 (m), 1611 (s), 1519 (s), 1433 (m), 1368 (s), 1289 (w), 1114 (w), 1068 (s), 1015 (w), 958 (w), 857 (m), 765 (m), 686 (w), 647 (m).

2.3. Preparation of $[Ni_2(L)(H_2O)_3(HBTC)_2]\cdot3.6H_2O$ (*2*)

A mixture of L (10.5 mg, 0.025 mmol), H_3BTC (6.3 mg, 0.03 mmol), $NiSO_4\cdot6H_2O$ (13.1 mg, 0.05 mmol) in solution of MeOH/H_2O (3 mL/5 mL) was adjusted to pH ≈ 5–8 using 0.5 mol L^{-1} NaOH solution. Then the mixture was sealed into a Teflon-lined stainless steel container and heated at 180 °C for 3 days. After being cooled to room temperature, aqua-blue block crystals of **2** were obtained in 85% yield based on H_3BTC. Anal. Calcd for $C_{42}H_{37.2}N_8O_{18.6}Ni_2$: C, 47.19; H, 3.51; N, 10.48%. Found: C, 47.08; H, 3.46; N, 10.42%. IR (KBr pellet, cm^{-1}): 3388 (m), 1619 (s), 1584(m), 1518 (s), 1434 (w), 1351 (m), 1285 (w), 1077 (m), 934 (m), 946 (w), 840 (w), 756 (m), 697 (m), 666 (m).

2.4. Preparation of $[Ni(L)(H_2O)_2](BPDC)\cdot2H_2O$ (*3*)

A mixture of L (10.5 mg, 0.025 mmol), H_2BPDC (12.1 mg, 0.05 mmol), $NiSO_4\cdot6H_2O$ (13.1 mg, 0.05 mmol) in MeOH (3 mL) and H_2O (5 mL) was adjusted to pH ≈ 7 with 0.5 mol L^{-1} NaOH solution. Then the mixture was sealed into a Teflon-lined stainless steel container and heated at 180 °C for 3 days. After cooling to room temperature, green pallet crystals of **3** were obtained in 30% yield based on L. Anal. Calcd for $C_{38}H_{34}N_8O_8Ni$: C, 57.82; H, 4.34; N, 14.19%. Found: C, 57.88; H, 4.28; N, 14.23%. IR (KBr pellet, cm^{-1}): 3168 (m), 1588 (s), 1542 (s), 1505 (s), 1362 (s), 1309 (m), 1261 (m), 1118 (w), 1066 (w), 1011 (w), 934 (w), 840 (w), 767 (m), 655 (m).

2.5. Preparation of $[Ni(L)(H_2O)(BPDC)]\cdot4H_2O$ (*4*)

Complex **4** was prepared by the same procedure used for preparation of **3** except that the ratio of L, H_2BPDC and $NiSO_4\cdot6H_2O$ was 1:2:4 rather than 1:2:2 used in preparation of **3**, and the weight of L is 10.5 mg (0.025 mmol). The mixture was adjusted to pH ≈ 7 with 0.5 mol L^{-1} NaOH solution. Green prism crystals of **4** were obtained in 70% yield based on L. Anal. Calcd for $C_{38}H_{36}N_8O_9Ni$: C, 56.53; H, 4.49; N, 13.88%. Found: C, 56.49; H, 4.45; N, 13.82%. IR (KBr pellet, cm^{-1}): 3367 (m), 1598 (s), 1583 (s), 1533 (s), 1504 (s), 1396 (s), 1376 (s), 1317 (w), 1247 (m), 1072 (m), 1014 (w), 958 (w), 829 (m), 771 (m), 719 (w), 673 (m).

2.6. Preparation of $[Ni_2(L)(MeOH)_4(BPDC)_2]\cdot2H_2O$ (*5*)

Complex **5** was obtained by the same procedure as that for **3** except that the ratio of L, H_2BPDC and $NiSO_4\cdot6H_2O$ was 1:1:1, and the weight of L is 10.5 mg (0.025 mmol). The mixture was adjusted to pH ≈ 7 with 0.5 mol L^{-1} NaOH solution. Light green crystals of **5** were obtained in 10% yield based on H_2BPDC. Anal. Calcd for $C_{56}H_{54}N_8O_{14}Ni_2$: C, 56.98; H, 4.61; N, 9.49%. Found: C, 56.92; H, 4.58; N, 9.43%. IR (KBr pellet, cm^{-1}): 3411 (m), 3122 (w), 1596 (s), 1527 (s), 1510 (s), 1398 (s), 1245 (w), 1128 (w), 1074 (m), 1018 (w), 935 (w), 781 (m), 680 (m).

2.7. Crystal structure determination

X-ray diffraction measurements for **1** and **2** were made on a Rigaku Raxis-Rapid II imaging plate area detector with Mo-Kα radiation (0.71075 Å) using MicroMax-007HF microfocus rotating anode X-ray generator at 200 K. The structures of **1** and **2** were solved by direct methods with *SIR92* and expanded using Fourier techniques by *DIRFID-99* [23]. The non-hydrogen atoms were refined anisotropically by the full matrix least-squares method on F^2. And hydrogen atoms were refined using the riding model. All calculations for **1** and **2** were performed using the *CrystalStructure* [24] crystallographic software package except for refinement, which was performed using *SHELXL* [25]. The crystallographic data collections for **3**–**5** were carried out on a Bruker Smart Apex CCD area detector diffractometer with graphite-monochromated Mo-Kα radiation (0.71073 Å) at 293(2) K using ω-scan technique. The diffraction data were integrated by using the *SAINT* program [26], which was also used for the intensity corrections for the Lorentz and polarization effects. Semiempirical absorption corrections were applied using *SADABS* program [27]. The structures were solved by direct methods using SHELXS-97 [28], and all of the non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the *SHELXL* crystallographic software package [25]. The hydrogen atoms except those of solvent molecules were generated geometrically and refined isotropically using the riding model. The details of the crystal parameters, data collection and refinements for the complexes are summarized in Table 1, and selected bond lengths and angles are listed in Table S1.

3. Results and discussion

3.1. Crystal structure of $[Zn_2(L)(BTC)(NO_3)]\cdot H_2O\cdot2CH_3CN$ (*1*)

The results of single crystal X-ray diffraction analysis reveal that the asymmetric unit of **1** consists of a half molecule of $[Zn_2(L)(BTC)(NO_3)]\cdot H_2O\cdot2CH_3CN$. As illustrated in Fig. 1a, Zn1 is