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Synthesis, structure and gas adsorption properties of coordination polymers based on mixed imidazole-containing ligands and carboxylate ligands

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Abstract

Herein, we report the synthesis of two novel coordination polymers using a combination of imidazole-containing ligands, namely 1,3,5-tris((1H-imidazol-1-yl)methyl)benzene (L¹) and 3,3',5,5'-tetra(1H-imidazol-1-yl)-1,1'-biphenyl (L²) and a carboxylate ligand derived from 4,4'-biphenyldicarboxylic acid (H₂BPDC). The structures of the two coordination polymers [Ni(L¹)(BPDC)]·2H₂O (1·2H₂O), which exhibits a 2-fold interpenetrated 3D \rightarrow 3D architecture, and {[Co(CH₃OH)₂(L²)_{0.5}(BPDC)] (2) possessing a 2D framework, have been determined. Moreover, the gas adsorption properties of **1** and **2** have been investigated.

Introduction

Metal organic frameworks (MOFs) have emerged as one of the most intriguing subjects in material science not only because of their fascinating topological structures but also due to their high surface areas and tunable pore size.^[1-3] After years of development, studies on MOFs have been expanded from mere synthesis to extensive applications in areas such as gas storage and separation, catalysis, energy storage, luminescent materials, drug delivery, magnetic materials and so on.^[4-15] Although quantities of MOFs have been successfully synthesized, controllable synthesis and fully predicting the structure remains a challenge.

According to previous studies, not only the nature of the building blocks (the

linkers and metal ion/clusters nodes) but also synthetic factors such as temperature, solvent, pH, templates and so on can play a pivotal role in the synthesis of MOFs.^[16-25] Among these influencing factors, rational design and choice of organic ligands are critical in the construction of MOFs.^[26] Furthermore, in addition to using a single ligand as a building block, a mixed-ligand strategy is often employed as well because it can combine the characters of different ligands and thus be beneficial for the construction of more complicated architectures.^[27-29]

As typical ligands with a strong capability of coordination, both imidazole-containing ligands and carboxylate ligands are the most commonly used organic linkers in the synthesis of MOFs. Herein, we report the synthesis of two novel coordination polymers by using the combination of imidazole-containing ligands and carboxylate ligands with the formula of $[Ni(L^1)(BPDC)] \cdot 2H_2O$ (1) and { $[Co(CH_3OH)_2(L^2)_{0.5}(BPDC)]$ (2) ($L^1 = 1,3,5$ -tris((1H-imidazol-1-yl)methyl)benzene; L² 3,3',5,5'-tetra(1H-imidazol-1-yl)-1,1'-biphenyl; = H₂BPDC = 4,4'-biphenyldicarboxylic acid, Scheme 1). The structures of these two complexes have been determined, with complex 1 exhibiting a 2-fold interpenetrated $3D \rightarrow 3D$ architecture, while complex 2 exhibits a 2D framework, where the carboxylate ligand BPDC²⁻ adopts a $\kappa^1 - \kappa^1 - \mu_2$ -BPDC mode to connect two Co(II) ions and are nearly parallel to the 2D L²-Co layers. Moreover, the thermal stability and sorption properties of the complexes have been investigated.



Scheme 1. Structures of L^1 , L^2 and H_2BPDC . Experimental Section

Materials and methods

The organic ligands L^1 and L^2 were synthesized by following a previously published procedure.^[30, 31] All other commercially available chemicals and solvents are of reagent grade and used without further purification. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C Elemental Analyzer at the analysis center of Nanjing University. FT-IR spectra were recorded in the range of 400 - 4000 cm⁻¹ on a Bruker Vector22 FT-IR spectrophotometer using KBr pellets. Powder X-ray diffraction (PXRD) measurements were carried out on a Bruker D8 Advance X-ray diffractometer using Cu-K α radiation ($\lambda = 1.5418$ Å), in which the X-ray tube was operated at 40 kV and 40 mA. Thermal gravimetric analyses (TGA) were taken on a Mettler-Toledo (TGA/DSC1) thermal analyzer under the N₂ atmosphere with a heating rate of 10 °C min⁻¹. The fluorescence spectra were measured on a Perkin Elmer LS-55 fluorescence spectrophotometer.

Synthesis of [Ni(L¹)(BPDC)]·2H₂O (1). A mixture of L¹ (16 mg, 0.05mmol), NiCl₂·6H₂O (47.5 mg, 0.2 mmol), *N*,*N*-dimethylformamide (DMF, 2 mL) and H₂O (8 mL) was sealed in Teflon-lined stainless steel container and heated at 90 °C for 4320 min. After being cooled to room temperature, green block crystals of **1** were obtained in 32% yield. Anal. Calcd for $C_{32}H_{30}NiN_6O_6$: C 58.82, H 4.60, N 12.86 %. Found: C 58.91, H 4.55, N 12.67%. IR (KBr pellet, cm⁻¹): 3062 (w), 1742 (m), 1710 (s), 1646 (s), 1480 (m), 1461 (w), 1433 (m), 1403 (s), 1220 (s), 1109 (s), 1108 (w), 1002 (w), 956 (w), 922 (w), 861 (w), 802 (m), 711 (m), 734 (w), 602 (w), 580 (w), 502 (m), 489 (m).

Synthesis of { $[Co(CH_3OH)_2(L^2)_{0.5}(BPDC)]$ (2). A mixture of L² (10.5 mg, 0.25 mmol), $Co(NO_3)_2$ ·6H₂O (29.1 mg, 1.0 mmol), *N*,*N*-dimethylformamide (DMF, 2 mL), CH₃OH (4 mL) and H₂O (4 mL) was sealed in Teflon-lined stainless steel container and heated at 120 °C for 4320 min. After being cooled to room temperature, pink block crystals of **2** were obtained in 29% yield. Anal. Calcd for $C_{28}H_{23}CoN_4O_6$: C 58.95, H 4.06, N 9.82 %. Found: C 58.91, H 4.12, N 9.76%. IR (KBr pellet, cm⁻¹): 3066 (w), 1782 (m), 1700 (s), 1622 (s), 1610 (m), 1555 (w), 1492 (m), 1465 (s), 1362 (s), 1355 (s), 1236 (w), 1101 (w), 1051 (w), 1022 (w), 958 (m), 874 (w), 865 (m), 735 (m), 732 (w), 681 (w), 602 (w), 584(m), 516 (m).

X-Ray crystallography

The crystallographic data collections for **1** and **2** were carried out on a Bruker Smart Apex II CCD area-detector diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 293(2) K using the ω -scan technique. The diffraction data were integrated by using the *SAINT* program ^[32], which was also used for the intensity corrections for the Lorentz and polarization effects. Semi-empirical absorption correction was applied using the *SADABS* program ^[33]. The structures were solved by direct methods and all the non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package ^[34]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the water molecules were located from the difference Fourier maps and refined with restraint of the O-H and H···H distance (0.96 Å and 1.52 Å, respectively). Other hydrogen atoms were introduced at the calculated positions. The details of the crystal parameters, data collection and refinements for the complexes are summarized in **Table 1**, and selected bond lengths and angles with their estimated standard deviations are listed in **Table 2**. CCDC NO. 2012894 (1), and 2012895 (2).

2 Complex 1 Formula C₃₂H₃₀NiN₆O₆ $C_{28}H_{23}CoN_4O_6$ Formula weight 653.33 570.43 T (K) 293(2) 293(2) Crystal system Monoclinic Orthorhombic Space group Fddd $P2_1/n$ a (Å) 14.970(4) 15.653(2) *b* (Å) 12.756(3) 23.218(4) *c* (Å) 16.397(4) 30.639(5) α (°) 90 90 90 β (°) 107.900(3) γ (°) 90 90 $V(Å^3)$ 2979.6(13) 11135(3) Ζ 4 16 D_{calc} (g cm⁻³) 1.456 1.361 μ (mm⁻¹) 0.707 0.664 *F*(000) 6860 1360 Reflections collected 15673 13480 Unique reflections 5854 2498 Goodness-of-fit on F^2 1.028 1.331 0.0805 0.1188 R_1 , $wR_2 [I > 2\sigma(I)]^{a,b}$ 0.1207 0.2170 R_1 , 0.1337 0.1242 0.1349 wR_2 [all data] 0.2196 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|. \ {}^{b}wR_{2} = |\Sigma w(|F_{o}|^{2} - |F_{c}|^{2})| / \Sigma |w(F_{o})^{2}|^{1/2}, \text{ where } w = m = 1 / [\sigma^{2}(F_{o})^{2} + (aP)^{2} + bP].$ $P = (F_o^2 + 2F_c^2)/3$

 Table 1. Crystal Data and Structure Refinements for complexes 1 - 2.

|--|

		1	
Ni(1)-O(4)#1	2.037(3)	Ni(1)-N(2)#3	2.086(4)
Ni(1)-N(6)	2.059(4)	Ni(1)-O(2)	2.106(3)
Ni(1)-N(4)#2	2.074(4)	Ni(1)-O(1)	2.200(3)
O(4)#1-Ni(1)-N(6)	89.12(14)	O(4)#1-Ni(1)-O(2)	174.35(13)
O(4)#1-Ni(1)-N(4)#2	86.84(14)	N(6)-Ni(1)-O(2)	95.25(14)
N(6)-Ni(1)-N(4)#2	94.94(15)	N(4)#2-Ni(1)-O(2)	89.22(13)

O(4)#1-Ni(1)-N(2)#3	94.06(14)	N(2)#3-Ni(1)-O(2)	89.39(14)		
N(6)-Ni(1)-N(2)#3	91.65(15)	O(4)#1-Ni(1)-O(1)	114.26(13)		
N(4)#2-Ni(1)-N(2)#3	173.36(15)	N(6)-Ni(1)-O(1)	156.62(13)		
N(2)#3-Ni(1)-O(1)	86.65(13)	N(4)#2-Ni(1)-O(1)	86.98(13)		
O(2)-Ni(1)-O(1)	61.43(12)				
2					
Co(1)-N(1)#1	2.108(6)	Co(1)-O(3)	2.110(6)		
Co(1)-N(1)	2.108(6)	Co(1)-O(1)	2.116(5)		
Co(1)-O(3)#1	2.110(6)	Co(1)-O(1)#1	2.116(5)		
N(1)#1-Co(1)-N(1)	93.3(3)	O(3)#1-Co(1)-O(1)	87.8(2)		
N(1)#1-Co(1)-O(3)#1	88.2(3)	O(3)-Co(1)-O(1)	88.1(3)		
N(1)-Co(1)-O(3)#1	178.1(3)	N(1)#1-Co(1)-O(1)#1	93.3(2)		
N(1)#1-Co(1)-O(3)	178.1(3)	N(1)-Co(1)-O(1)#1	90.6(3)		
N(1)-Co(1)-O(3)	88.2(3)	O(3)#1-Co(1)-O(1)#1	88.1(3)		
O(3)#1-Co(1)-O(3)	90.3(4)	O(3)-Co(1)-O(1)#1	87.8(2)		
N(1)#1-Co(1)-O(1)	90.6(3)	O(1)-Co(1)-O(1)#1	174.3(3)		
N(1)-Co(1)-O(1)	93.3(2)				

Symmetry transformations used to generate equivalent atoms: #1 x-1, y, z; #2 x-1/2, -y+3/2, z-1/2; #3 x, y+1, z for 1; #1 -x+1/4, -y+1/4, z for 2.

Results and discussion

Crystal structure description

Crystal Structure of [Ni(L¹)(BPDC)]·2H₂O (1). Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in the monoclinic crystal system with the space group of $P2_1/n$. Each asymmetric unit consists of one Ni(II) cation, one L¹ ligand, one BPDC²⁻ anion and two free water molecules. As depicted in **Figure 1a**, the Ni1 atom adopts an octahedral coordination geometry surrounded by three nitrogen atoms (N2#1, N4#2, N6) from three distinct imidazole-containing ligands L¹ and three oxygen atoms (O1, O2, O4#3) from two adjacent carboxylate ligands. The Ni-O and Ni-N bond lengths are in the range of 2.037(3) - 2.200(3) and 2.059(4) - 2.086(4) Å, respectively. Further inspection of the structure of **1** reveals that each L¹ binds to three Ni(II) atoms to form a two-dimensional (2D) networks (**Figure 1b**) by ignoring the connection between Ni(II) and BPDC²⁻ anions. Moreover, the carboxylate groups in each BPDC²⁻ adopt a (κ^1)-(κ^2)- μ_2 -BPDC coordination mode to connect two Ni(II) atoms, which pillar the 2D L¹-Ni networks to give a 3D framework (**Figure 1c**). The most striking feature of compound **1** is that a pair of identical 3D frameworks is interlocked with each other by non-covalent interactions (**Figure 1e**), which thus directly result in the formation of a 2-fold interpenetrated $3D\rightarrow 3D$ architecture (**Figure 1d**). From a topological viewpoint, the L¹ ligands connect three Ni(II) ions, and thus can be regarded as 3-connected nodes, while the BPDC²⁻ links two Ni(II) and can be simplified to 2-connected nodes. Meanwhile, Ni(II) can be treated as 5-connectors since Ni(II) links three L ligands and two BPDC²⁻. According to the simplification rule, the overall structure of **1** is a 3,5-connected 2-nodal 3D net with stoichiometry (3-c)(5-c), as shown in **Figure 1g** and **1h**. The Point (Schlăfli) symbol for the 3D net is $\{6^3\}$ $\{6^9.8\}$ calculated by the TOPOS program ^[35, 36].



Figure 1. (a) The coordination environment of Ni(II) in **1** with the ellipsoids drawn at the 30% probability level. The hydrogen atoms are omitted for clarity. Symmetric code: #1: x, 1+y, z; #2: -0.5+x, 1.5-y, -0.5+z; #3: -1+x, y, z. (b) The 2D L¹- Ni networks and (c) the 1D BPDC-Co chains in **1**. (d) The 3D framework pillared by BPDC²⁻. (e) The detailed non-covalent interactions between the interpenetrated 3D framework. (f) The final 2-fold

interpenetrated structure of **1**. Schematic representation of (3,5)-connected single 3D framework (g) and (h) 2-fold interpenetration framework of **1**.

Crystal Structure of $\{[Co(CH_3OH)_2(L^2)_{0.5}(BPDC)]\}$ (2). Single-crystal X-ray diffraction analysis reveals that 2 crystallizes in the orthorhombic crystal system with space group of *Fddd*. Each asymmetric unit contains one half of the molecular formula of complex 2. As depicted in Figure 2a, Co1 atom adopts an octahedral coordination geometry surrounded by two nitrogen atoms (N1, N1#1) from two adjacent imidazole-containing ligands L² and four oxygen atoms (O1, O1#1, O3, O3#1) from two distinct carboxylate ligands and two coordinated methanol molecules. The Co-N bond length is 2.106(7) Å and the Co-O bond lengths are 2.110(7) and 2.115(5) Å, respectively. In the structure of 2, each L^{2s} connects four Co(II) ions and these four Co(II) ions are almost in the same plane, which thus results in the formation of a two-dimensional (2D) L²-Co networks (Figure 2b) by ignoring the connection between Co(II) and BPDC²⁻ anions. Furthermore, it is worth noting that although the carboxylate groups in each BPDC²⁻ connect two Co(II) atoms in (κ^1) - (κ^1) - μ_2 -BPDC coordination mode to give 1D BPDC-Co chains (Figure 2c), these chains are parallel to the 2D L²-Co networks and are located at both two sides of the plane, which then generates the 2D sandwich layer structure (Figure 2d). Finally, the 3D supramolecular architecture of 2 (Figure 2f) is obtained through the noncovalent interlayer interactions including hydrogen interactions (2.315 Å) and π ... π interactions (3.768 Å) [37] between L² and BPDC²⁻ (Figure 2e). According to the simplification rule, the overall structure of 2 is 4,4-connected 2-nodal 3D net with stoichiometry $(4-c)_2(4-c)$, as shown in Figure. 2g and 2h.



Figure 2. (a) The coordination environment of Co(II) in **2** with the ellipsoids drawn at the 30% probability level, the hydrogen atoms are omitted for clarity. Symmetric code: #1: 0.25-x, 0.25-y, z; #2: -0.75-x, 0.25-y, z; #3: x, 0.75-y, 0.75-z; #4: 0.75-x, y, 0.75-z; #5: 0.75-x, 0.75-y, z. (b) The 2D L²-Co(II) networks and (c) the 1D BPDC-Co(II) chains in **2**. (d) The 2D sandwich L²-BPDC-Co(II) layers in **2**. (e) The non-covalent interlayer interactions. (f) The final 3D supramolecular structure of **2**. Schematic representation of (4,4)-connected single 2D framework (g) and (h) 3D framework by non-covalent of **2**.

Powder X-Ray Diffraction (PXRD) and Stability Studies

The bulk-phase purity of the synthesized samples of **1** and **2** was examined by using PXRD measurements. As depicted in **Figure 3**, the results of PXRD analysis revealed that the peak positions of the obtained crystalline samples of **1** and **2** were consistent with the simulated ones generated from the single-crystal diffraction data, confirming the phase purity of the synthesized samples. Differences between the patterns can be

attributed to differences in the wavelength (Cu radiation for PXRD, Mo for SCXRD) of the incident X-radiation. Difficulties associated with the characterization of as synthesized MOFs have been discussed recently.^[38]



Figure 3. PXRD patterns for 1-2 under ambient conditions: simulated (black) and as-synthesized (red).

The thermal stability of **1** and **2** was investigated by thermogravimetric analysis (TGA). As shown in **Figure 4**, compound **1** displays a weight loss of 5.7 % in the range of $30 - 160^{\circ}$, suggesting the release of the free water molecules (calcd 5.52%) and its framework begins decomposing at about 415. Complex **2** exhibits a weight loss of 11.2 % from 30 to 150 °, corresponding to the release of the free and coordinated water molecules and the structure remains stable up to 390 °.



Figure 4. The TGA curves of 1 and 2.

Gas adsorption properties

The results of the structural analyses show that there are solvent molecules in the complexes 1 and 2. Further TGA and PXRD measurements were carried out to ascertain the thermal stability of the complexes for subsequent sorption property investigations, and it was found that the solvent molecules in 1 and 2 can be removed completely by heating to give dehydrated samples of 1' and 2' without destroying the structure (Figure S2 and S3), respectively. The vapor adsorption behavior of 1' and 2' was investigated with N₂, H₂O and MeOH. As shown in Figure 5, the sorption curves of N_2 at 77 K for 1' and 2' suggest only surface adsorption. ^[39-41] The final value of the H₂O uptake is about 83 cm³ g⁻¹ (67 mg g⁻¹) corresponding to 2.3 H₂O molecules per formula unit, while the uptake of MeOH is about 49 cm³ g⁻¹ (70 mg g⁻¹) equivalent to 1.1 MeOH molecules per formula unit of 1'. As for the adsorption of 2', the uptake is about 41 cm³ g⁻¹ (33 mg g⁻¹) for H₂O and 91 cm³ g⁻¹ (130 mg g⁻¹) for MeOH (Figure 5b), corresponding to 0.98 H₂O, 2.19 and MeOH molecules per formula unit, respectively. Based on above results, it is observed that the complex 1' has the adsorption abilities of H₂O over MeOH vapor, while 2' exhibits larger uptake for MeOH than water, the reason can be attributed to the kinetic diameter of MeOH (3.6 -4.0 Å) is higher than that of water (2.6 -2.9 Å). Thus, most of the reported MOFs show larger water sorption than MeOH.



Figure 5. N_2 , MeOH and H_2O sorption isotherms for 1' (a) and 2' (b) (filled shape $\mathbf{\nabla}$, adsorption; open shape O, desorption).

Conclusion

In summary, two novel coordination polymers have been synthesized successfully using the mixed-ligand strategy by employing imidazole-containing ligands and carboxylate ligands under the solvothermal conditions. Both of the structure of complexes 1 and 2 exhibit 3D coordination framework architecture with different topologies. With the assistance of non-covalent interactions, 1 exhibits a 2-fold interpenetrated 3D structure, while complex 2 possesses a 2D framework. The results imply that both auxiliary ligands and anions can impact on the structure of the coordination polymers. The results of gas adsorption demonstrate that the frameworks show unique adsorption properties towards H_2O and MeOH, implying a potential application in vapor separation.

Acknowledgements

This work was supported by the Basic Research Program of Shenzhen (JCYJ20190812151405298, JCYJ20170413153034718 & JCYJ20170818164040422), CAS Key Laboratory of Health Informatics (2011DP173015) and CR thanks the EPSRC for an Overseas Travel Grant (EP/R023816/1).

Supplementary materials

CCDC NO. 2012894 - 2012895 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

Conflicts of interest

There are no conflicts to declare.

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