Introduction

In recent years, reasonable design and controllable syntheses of metal-organic coordination polymers have gained a significant interest due to their important application prospects.1–5 During the controlled synthesis of coordination polymers, some important factors such as the reaction temperature,6,7 the solvent species,8,9 the ligand geometry,10 the pH of the solution11,12 and the presence of ancillary ligands13,14 can have profound effects on the crystal structures and self-assembly properties. In addition, the geometry and substituents on the ligands15–17 can change the frameworks of coordination polymers, and the shape and size of the cavities. With respect to stable network framework, ligands with different configurations will display multiple spatial orientations when they are coordinated to metal ions and accordingly will generate diverse structures. For ligands with elastic structures,18,19 their spatial configuration is prone to distortion when they occupy different coordination environments. However, rigid ligand configurations20,21 cannot usually be deformed in different reaction media or different coordination modes. The angle between the functional groups on the ligand will influence the spatial orientation of coordination polymerization, with different network structures generally being controlled by the steric aggregation structures of the ligands. Therefore, a change of spatial structure of the ligand will result in an obvious transformation of

Structural diversity induced by ligand geometry: From two-dimensional to three-dimensional coordination polymers with pyridine

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Abstract

Two coordination polymers with two-dimensional and three-dimensional structures are, \([\{\text{Zn}_3\text{(bdc)}_3\text{(py)}_2\}\cdot2\text{NMP}\}_n\) (1) \((\text{H}_4\text{bdc} = 1,4\text{-benzenedicarboxylic acid})\) and \([\text{Zn}_2\text{(NO}_3\text{)}_2\text{(btc)}\text{(nmp)}_2\text{(py)}]\}_n\) (2) \((\text{H}_3\text{btc} = 1,3,5\text{-benzenetricarboxylic acid})\), synthesized by hot-solution reactions of \(\text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\), pyridine (py) and two different ligands in N-methylpyrrolidone (NMP). \([\{\text{Zn}_3\text{(bdc)}_3\text{(py)}_2\}\cdot2\text{NMP}\}_n\) exhibits two-dimensional networks with trizinc subunits \([\text{Zn}_3\text{(COO)}_6\text{py}_2]\) stacking with a layer-by-layer alignment, and there are strong \(\pi\)--\(\pi\) interactions involving py from adjacent layers. \([\text{Zn}_2\text{(NO}_3\text{)}_2\text{(btc)}\text{(nmp)}_2\text{(py)}]\}_n\) has a three-dimensional structure containing two independent zinc ions, tetrahedral \(\text{ZnO}_4\) and octahedral \(\text{ZnNO}_5\). Based on X-ray studies, the coordination polymers \([\{\text{Zn}_3\text{(bdc)}_3\text{(py)}_2\}\cdot2\text{NMP}\}_n\) (1) have a porous structure with NMP guest molecules. In contrast, X-ray studies revealed that coordination polymer \([\text{Zn}_2\text{(NO}_3\text{)}_2\text{(btc)}\text{(nmp)}_2\text{(py)}]\}_n\) (2) had a larger void that was inhabited by coordinated py and NMP. In addition, the form of the two coordination polymers changed from two-dimensional to three-dimensional with transformation of the ligand geometry.

Keywords

coordination polymers, crystal structure, ligand geometry, pyridine, synthesis

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the coordination polymer structure in three-dimensional space. Furthermore, ancillary ligands may play an extremely important role on the process of structural assembly between metal ions and ligands, with examples including nitrogen donor ligand such as ammonium salts, pyridine, pyrazole, and pyrazine.\textsuperscript{22–24} Solvent molecules, such as H\textsubscript{2}O and C\textsubscript{2}H\textsubscript{5}OH demonstrate a stronger coordination ability compared to a carboxyally oxygen atom, or preferentially occupy the coordination vacancies due to metal ions.

We have systematically investigated the influence of the reaction temperature, mixed solvents, and ligand substituents on the crystal structures of various products.\textsuperscript{15,25,26} In this paper, we have synthesized two coordination polymers with two-dimensional (2D) and three-dimensional (3D) structures by hot-solution reactions of Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, pyridine (py), and two different ligands in NMP. The two products, {[Zn\textsubscript{n}(bdc)\textsubscript{n}(py)\textsubscript{2}·2NMP]\textsubscript{n}} (\textsuperscript{1}) (H\textsubscript{2}bdc = 1,4-benzenedicarboxylic acid) and [Zn\textsubscript{n}(NO\textsubscript{3})\textsubscript{n}(btc)(nmp)(py)]\textsubscript{n} (\textsuperscript{2}) (H\textsubscript{3}btc = 1,3,5-benzenetricarboxylic acid), are synthesized from Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O and py (pyridine), with the two ligands possessing different geometries in NMP (Scheme 1). The results indicate that a change of the spatial configuration of the ligands can have a profound effect on the structure of the coordination polymers with a change in the geometry from 2D to 3D being observed.

**Results and discussion**

*Descriptions of the crystal structures*

\[\text{[Zn}_{\text{n}}(\text{bdc})_{\text{n}}(\text{py})_{\text{2}}\cdot\text{2NMP}]_{\text{n}}\text{ (1)}\text{ consists of two independent zinc(II) cations, Zn1 is located in a distorted square-pyramidal geometry coordinated with four oxygen atoms from three carboxylates and a nitrogen atom from py; Zn2 lies in a distorted octahedral geometry coordinated with six oxygen atoms from six carboxylates. In addition, there are two bridge-link modes (\(\mu\)2- and \(\mu\)3-) in the carboxylates. The trinuclear zinc subunits consist of an octahedral ZnO\textsubscript{6} sandwich with two square-pyramidal units ZnO\textsubscript{4} (Figure 1(a)). In the ac plane, each trinuclear zinc subunit is further linked by six bdc units with adjacent six trinuclear zinc subunits to form a 2D-layered structure with a (3, 6) framework (Figure 1(b)). Along the b axis, the 2D framework stacking as parallel aligned mode, there are stronger \(\pi\)–\(\pi\) interactions between the py rings from adjacent layers, and guest NMP molecules located in the gap between layers (Figure 2).*

\[\text{[Zn}_{\text{n}}(\text{NO}_{\text{3}})_{\text{n}}(\text{btc})(\text{nmp})(\text{py})]_{\text{n}}\text{ (2)}\text{ consists of two independent zinc(II) cations. Zn1 lies in a tetrahedral geometry coordinated with three oxygen atoms from three btc units and one oxygen atom from nitrate; while Zn2 is located in an octahedral geometry with three oxygen atoms from three btc units, two oxygen atoms from two NMP molecules and a nitrogen atom from a py molecule. Every two zinc ions Zn1 and Zn2 are linked by three carboxylates (Figure 3(a)). To fill in the gaps left by the network skeleton, py is located*

![Scheme 1. The formation of coordination polymers 1 and 2 tuned by the geometry of the ligands.](image)

![Figure 1. (a) The trinuclear zinc subunits, and (b) the 2D (3, 6) framework of complex 1.](image)

![Figure 2. 2D view of the (3, 6) framework of 1 along the b axis.](image)
in a vertex of octahedral and two NMP molecules lie in neighbor two apex in a quadrangular plane, it can further enhance the stability of the structure. The three carboxylates of the btc ligand bridge three tetrahedral ZnO₄ and three octahedral ZnO₅N units, respectively (Figure 3(b)). Along the b axis, four zinc ions (two Zn1 and two Zn2) are linked by btc in a different direction to expand the 3D network (Figure 4), and cubeform voids in the 3D network can accommodated two nmp and a py that coordinate to Zn2.

The different geometries of the ligands, that is, line-type and triangle-type, result in the different 2D and 3D structures of products 1 to 2. Furthermore, the previously reported one-dimensional chain compounds, {[Zn(ip)(py)₂]·NMP}ₙ was synthetized using zinc nitrate, pyridine, and isophthalic acid (V-type ligand). The structural difference between these three compounds is clearly related to the geometry of the ligands (Table 1). In the three structures, py can show different coordination abilities because of the change of the geometry of the ligands. There are more obvious differences in the characteristics of the three structures on increasing the number of coordinated the zinc ions (4, 5, 6) and the connected number of carboxylates (1, 2, 3), while the number of py groups (0, 1, 2) coordinated with zinc ions decreases. Compound 1 has a high porosity (33.6%) due to the solvent molecules NMP occupying pores. This indicates that the subunits in the three compounds are well-regulated changes of the ligands, such as mononuclear zinc for ip, trinuclear zinc for bdc and tetranuclear zinc for btc. Therefore, we can conclude that the geometries of the ligands play very important roles in the self-assembly of the coordination polymers.

Conclusion

In summary, we have successfully synthesized two coordination polymers 1 and 2 with 2D and 3D structures, respectively. One coordination polymer 1 is a 2D (3, 6) framework with trinuclear zinc subunits, and the other polymer 2 is a 3D framework with tetranuclear zinc based on zinc(II). Compared with our previous reports, the results show that there are obvious influences of the geometries of the ligands on the structures of the coordination polymers originated from the different types of carboxylate (H₂ip, H₂bdc, and H₃btc).

Experimental procedures

Materials and methods

All chemicals employed in the reaction process were analytical grade, and were directly used without further purification. Infrared spectra were obtained on a Nicolet AVATAR FTIR 360 spectrometer as KBr presser. Elemental analysis was performed on a CE instruments EA-1110 elemental analyzer.

Syntheses

[Zn₃(bdc)₃(py)₂·2NMP]ₙ (1). H₂bdc (1 mmol, 166 mg) and Zn(NO₃)₂·6H₂O (1 mmol, 298 mg) were added to a 25-mL conical flask, then NMP (8 mL) was added and the mixture was stirred vigorously. Next, py (0.5 mL) was added drop-wise to the reaction mixture. The mixture was heated from 30 °C to 90 °C over 5 h and then kept at 90 °C for 72 h. Finally, the temperature was slowly reduced to room temperature over 10 h through programmed temperature control. Colorless block crystals (0.165 g, 47%) were obtained. Crystal suitable for X-ray diffraction were separated by filtration, washed with distilled water, and dried in air. Anal. calcd for Zn₃C₄₄H₃₆N₄O₁₄: C, 50.57; H, 3.48; N, 5.38; found: C, 49.89; H, 3.39; N, 5.17%. FTIR (KBr, cm⁻¹): 3449 (w), 2978 (w), 2927 (w), 1591 (vs), 1404 (vs), 1346 (m), 1285 (w), 1192 (w), 1037 (w), 847 (s), 797 (vs), 764 (s), 626 (w), 552 (m).

[Zn₂(NO₃)₂(btc)·2NMP]ₙ (2). Compound 2 was prepared by a similar method to compound 1, except that H₂bdc was replaced by H₃btc (1 mmol, 210 mg). Colorless block crystals (34 mg, 10%, based on Zn(NO₃)₂·6H₂O) were obtained. Crystal suitable for X-ray single-crystal diffraction were isolated by filtration, washed with distilled water, and dried in air. Anal. calcd for Zn₂C₂₄H₂₂N₄O₁₁: C, 42.56; H, 3.28; N,
Table 1. Comparison of the structural characteristic of the three coordination polymers.

| Coordination polymer | Coordination number of Zn$^{2+}$ | Zn$^{2+}$/COO$^-$ | PY/Zn$^{2+}$ | Guest/coordination number of nmp | Void (%) | Dimension |
|----------------------|-----------------------------------|------------------|--------------|----------------------------------|----------|-----------|
| [{Zn(ip)(py)$_2$}·NMP]$_n$ | 4 | 1 | 2 | 1/0 | 33.8 | 1 |
| [{Zn$_3$(bdc)$_3$(py)$_2$}·2NMP]$_n$ | 6, 5 | 3, 2 | 2 | 1, 0 | 1/0 | 33.6 | 2 |
| [Zn$_2$(NO$_3$)$_3$(btc)(nmp)$_2$(py)]$_n$ | 6, 4 | 2 | 1 | 0/2 | 0 | 3 |

Table 2. Crystal data and details of the data collection and refinement for complexes 1 and 2.

| Complex | 1 | 2 |
|---------|---|---|
| Empirical formula | Zn$_3$C$_{44}$H$_{40}$N$_4$O$_{14}$ | Zn$_2$C$_{24}$H$_{26}$N$_4$O$_{11}$ |
| Formula weight | 1044.91 | 677.23 |
| Temperature (K) | 223(2) | 298(2) |
| Crystal size (mm) | 0.32×0.30×0.27 | 0.35×0.35×0.26 |
| Crystal system | Monoclinic | Orthorhombic |
| Space group | P2$_1$/n | P2$_1$2$_1$2$_1$ |
| a (Å) | 15.0307 | 13.4769 |
| b (Å) | 9.6447 | 13.8960 |
| c (Å) | 15.9221 | 15.2742 |
| α (°) | 90 | 90 |
| β (°) | 107.680 | 90 |
| γ (°) | 90 | 90 |
| V (Å$^3$) | 2199.15 | 2860.5 |
| Z | 4 | 4 |
| D$_{calcd}$ (mg/m$^3$) | 2.1578 | 1.741 |
| μ (mm$^{-1}$) | 1.696 | 1.741 |
| F(000) | 1068 | 1384 |
| Refine unique | 5138 | 6699 |
| R(int) | 0.0325 | 0.0353 |
| Data/restraints/parameters | 5138/0/296 | 6699/0/372 |
| R$_1$ (I > 2σ(I)) | 0.0353 | 0.0457 |
| wR$_2$ (all data) | 0.1082 | 0.1182 |
| Goodness-of-fit on F$^2$ | 0.975 | 1.010 |
| Max./min., Δρ (e·Å$^3$) | 0.647/−0.531 | 0.945/−0.404 |
| Completeness | 99.8 | 100.0 |

Table 3. Selected bond lengths and angles for the two coordination polymers (in Å and °).

\[
\begin{align*}
&\text{[(Zn$_3$(bdc)$_3$(py)$_2$)·2NMP]$_n$ (1)} \\
&\text{Symmetry codes: } a=x+1/2, y+3/2, z+1/2; b=-x+2, -y+2, -z; c=-x+3/2, y-1/2, -z-1/2.
\end{align*}
\]

\[
\begin{align*}
&\text{Zn1-O1 1.972(2) Zn2-O5 2.191 O2-Zn2-O5b 90.44 O3c-Zn2-O5b 90.67} \\
&\text{Zn1-O4a 1.940(2) Zn2-O5b 2.191 O2b-Zn2-O3a 85.03 O4a-Zn1-O1 114.57} \\
&\text{Zn1-O5 2.016(2) O1-Zn1-O5 96.27 O2-Zn2-O3c 94.97 O4a-Zn1-O5 112.93} \\
&\text{Zn1-O5 2.479(2) O1-Zn1-O6 147.53 O2-Zn2-O5 90.44 O4a-Zn1-O5 112.93} \\
&\text{Zn1-N1 2.021(3) O1-Zn1-N1 97.91 O2-Zn2-O5b 89.56 O4a-Zn1-N1 104.65} \\
&\text{Zn2-O2 2.036(2) O2-Zn2-O2b 180.0 O3a-Zn1-O5 90.67 O5-Zn2-O5b 180.00} \\
&\text{Zn2-O2b 2.036(2) O2-Zn2-O3a 94.97 O3a-Zn2-O5b 89.33 O5-Zn1-O6 57.35} \\
&\text{Zn2-O3a 2.056(2) O2-Zn2-O3c 85.03 O3c-Zn2-O3a 180.0 O5-Zn1-O6 132.64} \\
&\text{Zn2-O3c 2.056(2) O2-Zn2-O5 89.56 O3c-Zn2-O5 89.33 O5-Zn2-O5b 89.51} \\
\end{align*}
\]

\[
\begin{align*}
&\text{[Zn$_2$(NO$_3$)$_3$(btc)(nmp)$_2$(py)]$_n$ (2)} \\
&\text{Symmetry codes: } a=-x-1, y+1/2, -z+3/2; b=-x-1/2, -y+1, z+1/2.
\end{align*}
\]

\[
\begin{align*}
&\text{Zn1-O1 1.958(3) Zn2-O8 2.105 O2-Zn2-O7 174.92 O6a-Zn2-O8 86.96} \\
&\text{Zn1-O3b 1.943(3) Zn2-N1 2.116 O2b-Zn2-O8 87.96 O6a-Zn2-N1 178.40} \\
&\text{Zn1-O5a 1.937(3) O1-Zn1-O9 92.85 O2b-Zn2-O4b 92.41 O7-Zn2-O4b 92.64} \\
&\text{Zn1-O9 2.021(4) O3b-Zn1-O1 117.56 O2-Zn2-O6a 90.87 O7-Zn2-O6a 88.44} \\
&\text{Zn2-O2 2.081(3) O3b-Zn1-O9 114.0 O2-Zn2-N1 90.40 O7-Zn2-O8 86.98} \\
&\text{Zn2-O4b 2.098(3) O5a-Zn1-O1 111.73 O4b-Zn2-O8 178.48 O7-Zn2-N1 90.21} \\
&\text{Zn2-O6a 2.096(3) O5a-Zn1-O3b 115.25 O4b-Zn2-N1 89.36 O8-Zn2-N1 92.11} \\
&\text{Zn2-O7 2.081(3) O5a-Zn1-O9 106.80 O6a-Zn2-O4b 91.56}
\end{align*}
\]

CCDC number 969395 and 969396 contain the supplementary crystallographic data for 1 and 2. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.
8.27; found: C, 42.03; H, 3.02; N, 7.96%. FTIR (KBr, cm\(^{-1}\)): 3456 (s), 2926 (w), 1616 (vs), 1470 (w), 1436 (vs), 1371 (vs), 1109 (w), 757 (m), 719 (s), 563 (w), 462 (w).

**X-ray crystallography**

Crystal data collection was carried out on Bruker SMART Apex CCD diffractometer with graphite monochromated MoK\(\alpha\) radiation (\(\lambda = 0.71073\) Å). Absorption corrections were applied using the multi-scan program SADABS.\(^{28}\) The structures were solved by direct methods, and non-hydrogen atoms were refined anisotropically by least-squares on \(F^2\) using the SHELXTL\(^{29}\) and SHELXL-97\(^{30}\) program packages. Crystallographic data, as well as details of data collection and refinement for the two compounds, are summarized in Table 2, and selected bond lengths and angles for the two crystal structures are listed in Table 3.

**Declaration of conflicting interests**

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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