

# Influence of hydrothermal synthesis temperature on the structures of two 3D coordination polymers

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## Abstract

Two 3D coordination polymers  $[\text{Zn}(\mu_4\text{-dmbdc})]_n$ , **1** and  $[\text{Zn}_5(\mu_3\text{-OH})_4(\mu_5\text{-dmbdc})_2(\mu_4\text{-dmbdc})]_n$ , **2** ( $\text{H}_2\text{dmbdc}$  = 2,5-dimethylbenzenedicarboxylic acid) have been prepared by hydrothermal syntheses with temperature as the only variable. The structure feature is the presence of monoatomic coordination bridges, i.e.  $\mu_3\text{-OH}$  and  $\mu_2\text{-O}$  (from  $\mu_3\text{-COO}^-$  of  $\mu_5\text{-dmbdc}$ ) in **2** synthesized at higher temperature. The coordination number of zinc ion and the bridging number of the carboxyl group increase with the increasing synthesis temperature, resulting in the formation of the more stable and condensed phase.

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**Keywords:** Coordination polymer; Hydrothermal synthesis; Temperature; Crystal structure

There is an extensive interest in the design and synthesis of functional inorganic/organic hybrid materials owing to their intriguing topologies and applications [1–19]. Hydrothermal synthesis is widely used in the preparation of such materials [6–19]. However, the control over the structures of the products in hydrothermal reactions is still a challenge. We and others have synthesized coordination polymers by hydrothermal reactions and found that temperature is a vital factor in determining the structures. The carboxyl groups of the benzene polycarboxylate ligands tend to combine more metal ions at elevated synthesis temperature, and the metal ions undergo hydrolysis during the reactions [12–19]. However, to the best of our knowledge, systematic studies on the role of hydrothermal synthesis temperature are rare [6–10]. Here, we report two 3D coordination polymers  $[\text{Zn}(\mu_4\text{-dmbdc})]_n$ , **1** and  $[\text{Zn}_5(\mu_3\text{-OH})_4(\mu_5\text{-dmbdc})_2(\mu_4\text{-dmbdc})]_n$ , **2** ( $\text{H}_2\text{dmbdc}$  = 2,5-dimethylbenzenedicarboxylic

acid) prepared by hydrothermal syntheses with temperature as the only variable.

In the structure of **1** prepared at the temperature below 150 °C [20,21], zinc ion is in slightly distorted tetrahedral coordination environment, being coordinated by four oxygen atoms from four  $\mu_4\text{-dmbdc}$  ligands. Each  $\mu_4\text{-dmbdc}$  connects four zinc ions with both of its two carboxyl groups in *syn-anti* bridging mode [22]. The discrete  $\text{ZnO}_4$  polyhedron is bridged by two pairs of  $\mu_2$  carboxyl groups to two adjacent polyhedra to form a chain along *c*-axis (Fig. 1a). The  $\text{ZnO}_4$  chain is further connected to four adjacent chains by  $\mu_4\text{-dmbdc}$  to form the 3D structure of **1** (Fig. 1b).

While prepared at the temperature higher than 170 °C, the structure of **2** is definitely different from that of **1**. The structure of **2** contains three crystallographically independent  $\text{Zn}^{2+}$  ions (Fig. 2): Zn1 is in slightly distorted octahedral coordination environment, being coordinated by two  $\mu_3\text{-OH}$  and four carboxyl oxygen atoms; Zn2 is also in slightly distorted octahedral environment, being coordinated by four  $\mu_3\text{-OH}$  and two carboxyl oxygen atoms; Zn3 is in distorted tetrahedral

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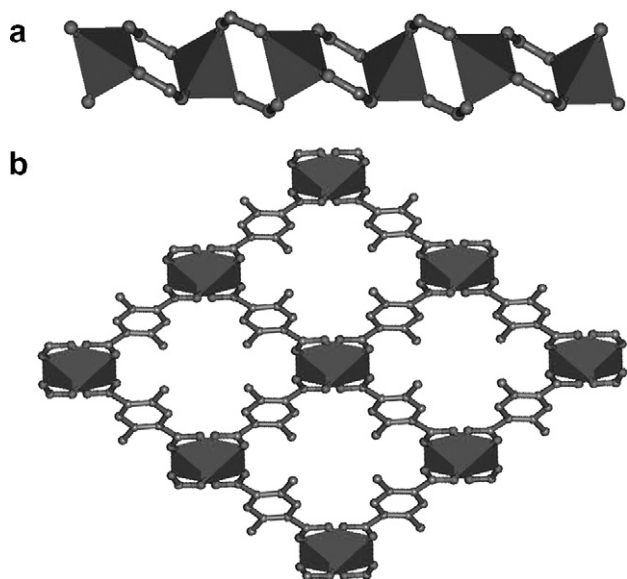


Fig. 1. (a) Polyhedron representation of the  $\text{ZnO}_4$  chain bridged by carboxyls in **1**. (b) A perspective view of the 3D structure of **1** along  $c$ -axis (hydrogen atoms are omitted for clarity).

environment, being coordinated by two  $\mu_3$ -OH and two carboxyl oxygen atoms. The  $\text{ZnO}_6$  octahedra and  $\text{ZnO}_4$  tetrahedra are joined together by  $\mu_3$ -OH,  $\mu_3$ - $\text{COO}^-$  and  $\mu_2$ - $\text{COO}^-$  to form a combined edge-sharing or corner-sharing  $\text{ZnO}_n$  chain extending along the  $a$ -axis (Fig. 3a). The  $\text{ZnO}_n$  chain is further connected to six adjacent chains to form the 3D structure of **2** (Fig. 3b).

X-ray powder diffraction measurements show that pure phases of **1** or **2** are obtained, respectively, with the same starting reaction mixture by changing only the hydrothermal synthesis temperature from 150 to 170 °C (Fig. 4). The structures of **1** and **2** are obviously determined by the synthesis temperature. The most significant change in the structure features is the presence of monoatomic coordination bridges, i.e.  $\mu_3$ -OH and  $\mu_2$ -O (from  $\mu_3$ - $\text{COO}^-$  of  $\mu_5$ -dmbdc) in **2** synthesized at higher temperature. Con-

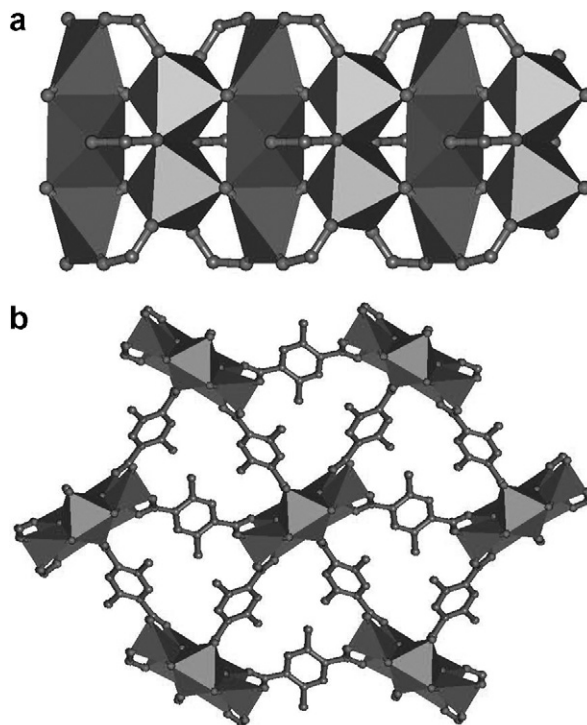


Fig. 3. (a) Polyhedron representation of  $\text{ZnO}_6$ ,  $\text{ZnO}_4$  combined chain in **2**. (b) A perspective view of the 3D structure of **2** along  $a$ -axis (hydrogen atoms are omitted for clarity).

sequently, the average coordination numbers of zinc ions increase from 4 to 5.33, and the average bridging numbers of  $\text{COO}^-$  also increase from 2 to 2.33. As a result, **2**, the more stable and condensed phase is formed with the numbers of  $\text{Zn}^{2+}/10^3 \text{ \AA}^3$  increasing from 4.08 to 6.00, and the densities increasing from 1.745 to 1.935  $\text{g/cm}^3$  (Table 1).

In summary, we have successfully synthesized two 3D coordination polymers  $[\text{Zn}(\mu_4\text{-dmbdc})_n]$ , **1** and  $[\text{Zn}_5(\mu_3\text{-OH})_4(\mu_5\text{-dmbdc})_2(\mu_4\text{-dmbdc})_n]$ , **2** at different hydrothermal synthesis temperatures. At higher temperature, monoatomic coordination bridges such as  $\mu_3$ -OH and  $\mu_3$ - $\text{COO}^-$

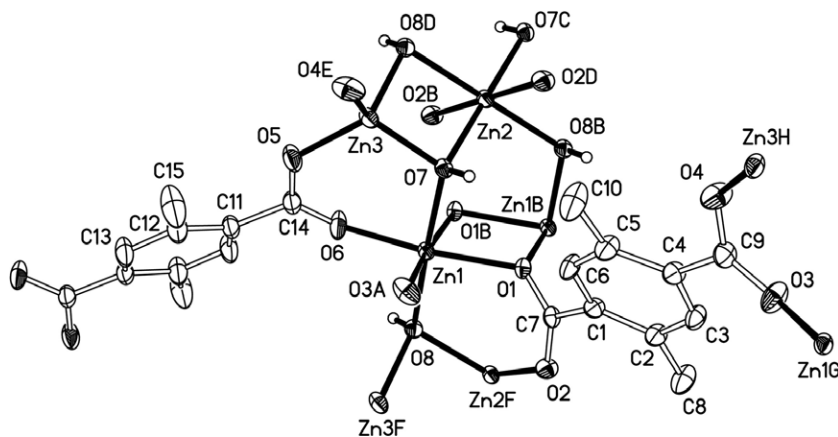


Fig. 2. ORTEP plot showing the coordination environments of zinc ions in **2**. (C–H hydrogen atoms are omitted for clarity). Symmetry codes: (a)  $-x + 1, y - 1/2, -z + 3/2$ ; (b)  $-x + 1, -y + 1, -z + 1$ ; (c)  $-x, -y + 1, -z + 1$ ; (d)  $x - 1, y, z$ ; (e)  $-x, y - 1/2, -z + 3/2$ ; (f)  $x + 1, y, z$ ; (g)  $-x + 1, y + 1/2, -z + 3/2$ ; (h)  $-x, y + 1/2, -z + 3/2$ .

Table 1  
Data for the structure features of **1** and **2**

Coordination polymer	Synthesis temperature	Monoatomic bridge	Coordination number/ $Zn^{2+}$	$Zn^{2+}/COO^-$	$Zn^{2+}/10^3 \text{ \AA}^3$	$D_{\text{calcd}}$ ( $\text{g}/\text{cm}^3$ )
<b>1</b> , $[Zn(\mu_4\text{-dmbdc})]_n$	150 °C	0	4	2	4.08	1.745
<b>2</b> , $[Zn_5(\mu_3\text{-OH})_4(\mu_5\text{-dmbdc})_2(\mu_4\text{-dmbdc})]_n$	170 °C	6	6, 6, 4	3, 2, 2	6.00	1.935

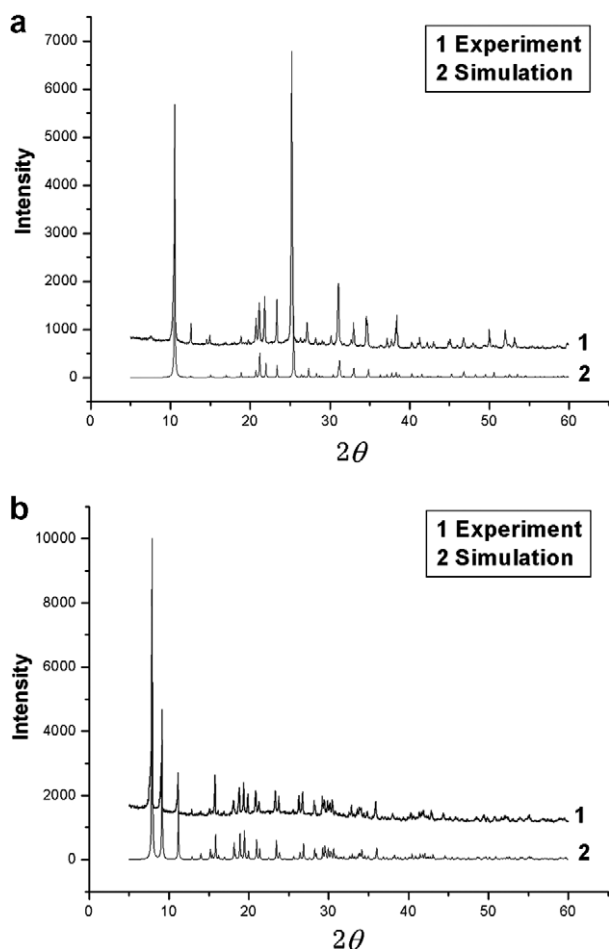


Fig. 4. Experimental and simulated X-ray powder diffraction patterns for **1** (a) and **2** (b).

combine metal ions and result in the increase of coordination number of metal ions and  $COO^-$  and the formation of the more condensed phase.

### Acknowledgments

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### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007.07.008.

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- [20] *Preparation for 1*: 2,5-dimethylbenzenedicarboxylic acid ( $H_2dmbdc$ , 0.097 g, 0.50 mmol) and NaOH (0.040 g, 1.0 mmol) were dissolved in  $H_2O$  (12 ml), nitric acid (2 mol/L) was slowly added to the solution until pH was adjusted to 7, then  $Zn(NO_3)_2 \cdot 6H_2O$  (0.15 g, 0.50 mmol) was added. The mixture was placed in a 20 ml Teflon-lined vessel, heated to 150 °C at the rate of 0.2 °C/min, and kept at 150 °C for 3 days, then slowly cooled down to room temperature at the rate of 0.1 °C/min. Colorless platelet crystals (0.040 g, yield 31%) were separated by filtration, washed with deionized water and dried in air. Elemental Analysis:  $C_{10}H_8O_4Zn$ , found (calcd) C 46.08 (46.64), H 3.07 (3.13)%. **2** was synthesized by a procedure similar to **1** only that the reaction temperature was changed from 150 to 170 °C. Colorless rod crystals (0.055 g, yield 57%) were collected by filtration. Elemental Analysis:  $C_{30}H_{28}O_{16}Zn_5$ , found (calcd) C 36.93 (37.09), H 2.95 (2.91)%.
- [21] Data collections for **1** and **2** were performed on a Bruker SMART Apex CCD diffractometer at 223 K. Absorption corrections were applied by using the multi-scan program SADABS. The structures were solved by direct methods, and non-hydrogen atoms were refined anisotropically by least-squares on  $F^2$  using the SHELXTL program.

Crystal data for **1**: Formula  $\text{ZnC}_{10}\text{H}_8\text{O}_4$ , monoclinic, space group  $C2/c$ ,  $a = 11.071(1)$ ,  $b = 14.068(2)$ ,  $c = 6.7041(7)$  Å,  $\beta = 110.106(2)^\circ$ ,  $V = 980.46(18)$  Å<sup>3</sup>,  $Z = 4$ ,  $R_1 = 0.0495$ ,  $wR_2 = 0.1148$ . Crystal data for **2**: Formula  $\text{Zn}_5\text{C}_{30}\text{H}_{28}\text{O}_{16}$ , monoclinic, space group  $P2_1/c$ ,  $a = 6.3061(3)$ ,  $b = 13.6926(6)$ ,  $c = 19.3122(9)$  Å,  $\beta = 91.491(1)^\circ$ ,  $V = 1666.98(13)$  Å<sup>3</sup>,  $Z = 2$ ,  $R_1 = 0.0241$ ,  $wR_2 = 0.0625$ . The detail crystallographic data for **1** and **2** have been deposited at the Cambridge Crystallographic Data Center as supplementary publication CCDC No. 650134 & 650135.

[22] Selected bond lengths (Å) and angles ( $^\circ$ ) for **1**: Zn–O 1.927(3), 1.942(3), O–Zn–O: 99.33(17), 109.71(13), 117.73(11), 103.37(18). **2**: Zn1–O1 2.124(1), Zn1–O6 2.055(2), Zn1–O7 2.058(1), Zn1–O8 2.036(1), Zn1–O1b 2.170(1), Zn1–O3a 2.056(1), Zn2–O7 2.073(1), Zn2–O2b 2.140(1), Zn2–O8b 2.130(1), Zn3–O5 1.922(2), Zn3–O7 1.967(1), Zn3–O4e 1.925(2), Zn3–O8d 1.974(1) Å; O1–Zn1–O7 86.54(5), O1–Zn1–O8

91.05(5), O1–Zn1–O1b 80.17(5), O1–Zn1–O3a 94.10(6), O6–Zn1–O7 92.58(6), O6–Zn1–O8 89.42(6), O6–Zn1–O1b 88.55(6), O6–Zn1–O3a 97.13(7), O7–Zn1–O3a 86.63(6), O7–Zn1–O1b 91.02(5), O8–Zn1–O1b 86.73(5), O8–Zn1–O3a 95.41(6), O7–Zn2–O2b 95.66(5), O7–Zn2–O2d 84.34(5), O7–Zn2–O8b 98.18(5), O7–Zn2–O8d 81.82(5), O7c–Zn2–O2b 84.34(5), O7c–Zn2–O2d 95.66(5), O7c–Zn2–O8b 81.82(5), O7c–Zn2–O8d 98.18(5), O8b–Zn2–O2b 96.84(5), O8b–Zn2–O2d 83.16(5), O8d–Zn2–O2b 83.16(5), O8d–Zn2–O2d 96.84(5), O5–Zn3–O7 111.71(6), O5–Zn3–O4e 103.41(7), O5–Zn3–O8d 121.37(7), O7–Zn3–O8d 88.63(5), O7–Zn3–O4e 123.29(7), O4e–Zn3–O8d 109.45(6), Zn1–O1–Zn1b 99.83(5), Zn1–O7–Zn2 118.05(6), Zn1–O7–Zn3 116.48(7), Zn2–O7–Zn3 95.82(6), Zn1–O8–Zn2f 117.96(6), Zn1–O8–Zn3f 118.36(7), Zn2f–O8–Zn3f 93.80(6). Symmetry codes: (a)  $-x + 1, y - 1/2, -z + 3/2$ ; (b)  $-x + 1, -y + 1, -z + 1$ ; (c)  $-x, -y + 1, -z + 1$ ; (d)  $x - 1, y, z$ ; (e)  $-x, y - 1/2, -z + 3/2$ ; (f)  $x + 1, y, z$ .