

Variable Architecture of Zinc Coordination Polymers

Modeled By Tetra-pyridinate Ligand With Different Anions

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Experimental sections

Materials and General Methods. All starting materials were obtained commercially and were used without further purification. Elemental analyses for C, H, N were performed on a Perkin-Elmer 240Q elemental analyzer. The IR spectra were recorded in range of 400-4000 cm⁻¹ on a Nicolet 5DX spectrometer (KBr pellets). The ligand TPOM was synthesized by a literature method.¹ Low-pressure N₂ adsorption measurements (up to 1 bar) were performed on Micromeritics ASAP 2020 M+C surface area and pore size analyzer.

Synthesis of {[Zn₂(TPOM₂)₂(Cl)₄]}_n (1). A mixture of ZnCl₂ (13mg, 0.1 mmol) and TPOM₂ (5.5mg, 0.025 mmol) was dissolved in 15 mL of CH₃CN. The final mixture was refluxed for 1 hours. Large bulk crystals were obtained from the filtrate. Yield of the reaction was ca. 15% based on TPOM₂. Anal. Calcd for C₅₀H₅₀Cl₈N₈O₉Zn₄: H 3.47%, C 41.36%, N 7.72%; found H 3.12%, C 40.96%, N 7.22%.

Synthesis of {[Zn₂(TPOM₂)(L1)₄]·4H₂O}_n (2). A mixture of Zn(OAc)₂ (18mg, 0.1 mmol), benzoic acid (8 mg, 0.05 mmol) and TPOM₂ (5.5mg, 0.025 mmol) was dissolved in 12 mL of CH₃OH/H₂O (1:5, v/v). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (25mL) under autogenous pressure and heated at 130°C for 3 days. Needle-like crystals were obtained, and crystals were filtered off, washed with mother liquid, and dried under ambient conditions. Yield of the reaction was ca. 41% based on TPOM₂. Anal. Calcd for C₅₃H₅₂N₄O₁₆Zn₂: H 4.63 %, C 56.25%, N 4.95% ; found H 4.11 %, C 56.76%, N 4.23%.

Synthesis of {[Zn₄(TPOM₂)(L2)₄]·guest}_n (3). A mixture of Zn(OAc)₂ (18mg, 0.1 mmol), H₂BDC (10 mg, 0.05 mmol) and TPOM₂ (5.5mg, 0.025 mmol) was dissolved in 12 mL of DMF/CH₃OH/H₂O (1:1:4, v/v/v). The final mixture was placed in a Parr Teflon-lined stainless

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steel vessel (25mL) under autogenous pressure and heated at 140°C for 3 days. Block-like crystals were obtained, and crystals were filtered off, washed with mother liquid, and dried under ambient conditions. Yield of the reaction was ca. 60% based on TPOM2. Anal. Calcd for dyhydrated $C_{57}H_{40}N_4O_{20}Zn_4$: H 2.96%, C 50.25%, N 4.11%; found H 3.45%, C 51.15%, N 4.99%.

Synthesis of $\{[Zn(TPOM)(Cl)_2]\}_n$ (4). The synthesis process is very similar to **1** except for TPOM. The final mixture was refluxed for 1 hours. Large bulk colorless-block crystals were obtained from the filtrate. Yield of the reaction was ca. 15% based on TPOM. Anal. Calcd for $C_{25}H_{24}Cl_2N_4O_4Zn$: H 4.17%, C 51.70%, N 9.65%; found H 3.92%, C 51.20%, N 9.22%.

Synthesis of $\{[Zn_2(TPOM)(L1)_4] \cdot 2H_2O\}_n$ (5). A mixture of $Zn(OAc)_2$ (18mg, 0.1 mmol), benzoic acid (8 mg, 0.05 mmol) and TPOM (5.5mg, 0.025 mmol) was dissolved in 12 mL of CH_3OH/H_2O (1:5, v/v). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (25mL) under autogenous pressure and heated at 120°C for 3 days. Needle-like crystals were obtained, and crystals were filtered off, washed with mother liquid, and dried under ambient conditions. Yield of the reaction was ca. 41% based on TPOM. Anal. Calcd for $C_{53}H_{48}N_4O_{14}Zn_2$: H 4.42 %, C 58.10%, N 5.11% ; found H 4.22 %, C 58.76%, N 5.35%.

Synthesis of $\{[Zn_2(TPOM)(L2)_2] \cdot 4H_2O\}_n$ (6). A mixture of $Zn(OAc)_2$ (18mg, 0.1 mmol), H_2BDC (10 mg, 0.05 mmol) and TPOM (5.5mg, 0.025 mmol) was dissolved in 8 mL of CH_3OH/H_2O (4:4, v/v). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (25mL) under autogenous pressure and heated at 140°C for 3 days. Block-like crystals were obtained, and crystals were filtered off, washed with mother liquid, and dried under ambient conditions. Yield of the reaction was ca. 60% based on TPOM. Anal. Calcd for dyhydrated $C_{57}H_{40}N_4O_{20}Zn_4$: H 4.13%, C 50.48%, N 5.74%; found H 4.42%, C 51.05%, N 5.89%.

X-Ray Structural Determination. X-ray diffraction data of **1** (0.25 × 0.2 × 0.15 mm), **2** (0.3 × 0.2 × 0.2 mm), **4** (0.25 × 0.15 × 0.1 mm), **5** (0.25 × 0.15 × 0.10 mm) and **6** (0.25 × 0.15 × 0.10 mm) were collected on Oxford Gemini S Ultra diffractometer using $Mo-K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation at room temperature , except for **3** (0.2 × 0.2 × 0.1 mm) using $Cu-K\alpha$ ($\lambda = 1.54178 \text{ \AA}$) radiation at 170 K . The structures of complexes were solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix leastsquares procedure based on F^2 values.² The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms.

The method of *SQUEEZE* in *PLATON* was carried out in the final crystal resolutions for **3** and **6**²¹.
CCDC-871661 (1), CCDC-871662 (2), CCDC-871663 (3), CCDC-871663 (4), CCDC-877830
(4), CCDC-877831 (5) and CCDC-877832 (6) contain the supplementary crystallographic data
for this paper. These data can be obtained free of charge from The Cambridge Crystallographic
Data Centre via <http://www.ccdc.cam.ac.uk/datarequest/cif>.

Reference:

- (1) Ryan, P. E.; Lescop, C.; Laliberté, D.; Hamilton, T.; Maris, T.; Wuest, J. D. *Inorg. Chem.* **2009**, *48*, 2793.
- (2) (a) Altomare, A.; Burla, M. C.; Camalli, M.; Casciarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, b115-119; b) G. M. Sheldrick, *SHELXL-97; Program for refinement of crystal structures*. University of Göttingen, Göttingen, Germany, **1997**.

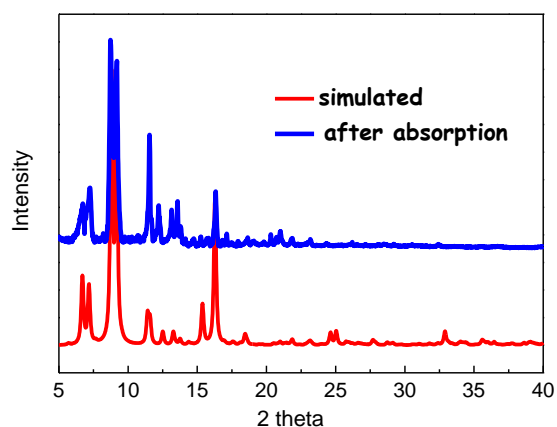


Figure S1. XRD spectrum of **3**

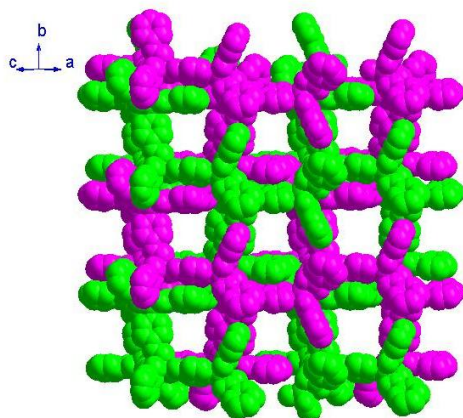


Figure S2. the packing mode of the 2-fold interpenetrating structure of **5**, showing the pores which were filled with isolated aqua molecules.