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Synthesis of Zinc Isonicotinates by Solid-state Reactions: A Green Route to Coordination Polymers

Jinxi Chen* and Ruobing Zhang
School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, P. R. China

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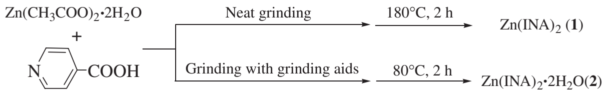
Two known coordination polymers, $Zn(INA)_2$ and $Zn(INA)_2 \cdot 2H_2O$ (INA: isonicotinate), have been synthesized through solid-state reactions that are more efficient and environmentally friendly than conventional methods. By varying the reaction conditions, the solid-state reactions between the metal salt and bridging ligand could be rationally controlled to give different polymeric three-dimensional structures or a mononuclear coordination compound.

Since the first rationally designed and synthesized coordination polymers were reported,[1] the preparative approaches to this class of materials have mainly relied on hydro(solvo)thermal synthesis, diffusion methods, and other approaches that are advantageous in the growth of high-quality single crystals.[2] As the primary motivation in crystal engineering shifted toward the design of functional materials for potential commercial applications, developing appropriate manufacturing routes has become an emerging challenge.[3] Compared to conventional solvent-based methods, solid-state synthesis is one of the most promising green chemistry approaches for being far more efficient, convenient, and environmentally friendly.[4] However, very limited success has been achieved in the synthesis of coordination polymers through the solid-state reaction strategy, and thus far few solid products of coordination polymers have been prepared and structurally ascertained by this means,[5] despite numerous coordination polymers reported. Herein we report the controlled synthesis of two known coordination polymers and a mononuclear coordination compound through solid-state reactions under different reaction conditions.

The reactions leading to $Zn(INA)_2$ (**1**) and $Zn(INA)_2 \cdot 2H_2O$ (**2**) are summarized in Scheme 1. In a typical synthesis, zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, 1.0 mmol) and isonicotinic acid (HINA, 2.0 mmol) were ground in an agate mortar with a pestle for 10 min, and the mixture was heated at 180 °C for 2 h to give a coordination polymer $Zn(INA)_2$ (**1**, CCDC-109338) (yield 96% based on ligand). A pungent odour was detected during the grinding and heating of the mixture, suggesting the release of acetic acid as a by-product. The structure of **1** was identified by a careful comparison of the experimental X-ray powder diffraction (XRPD) patterns with simulated ones from its single-crystal structure (Figure 1a) reported by Evans et al.,[6] which was synthesized solvothermally after treating $Zn(ClO_4)_2 \cdot 6H_2O$ with 4-cyanopyridine at 130 °C for 48 h. Gratifyingly, grinding the two reactants together in the presence of poly(ethylene glycol)-400 (PEG-400) or oleic acid as grinding aids, and then heating the mixture at 80 °C for 2 h, a different coordination polymer, $Zn(INA)_2 \cdot 2H_2O$ (**2**, CCDC-188415)[7] with some starting materials (see Figures S1 and S2 in Supporting Information[11]) was obtained. After a simple wash with ethanol, phase-pure product **2** was collected (yield 93%) and was structurally ascertained by comparison of the experimental with the simulated XRPD patterns for its single-crystal structure (Figure 1b). The two three-dimensional coordination polymers **1** and **2** have diamond- and quartz-like structures, respectively. The morphology was characterized by scanning electron microscopy (SEM, Figure S3[11]).



Scheme 1. Solid-state reactions between $Zn(CH_3COO)_2 \cdot 2H_2O$ and isonicotinic acid.

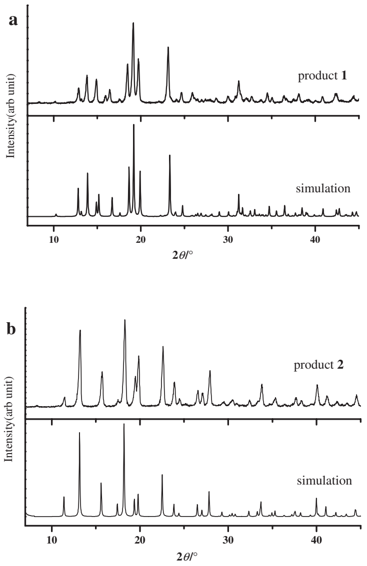


Figure 1. Comparison of XRPD patterns of product **1** (a) and **2** (b) with their respective calculated ones from single-crystal data.

In the neat grinding synthesis, when methanol treatment (immersed in methanol and then dried at 40 °C) was used after 10 min of grinding instead of heating at 180 °C for 2 h, the coordination polymer **1** was also obtained. On the other hand, if HINA was added to the solution of $Zn(CH_3COO)_2 \cdot 2H_2O$ in methanol, stirred for 2 h, and then dried at 40 °C, a mononuclear coordination compound, $Zn(INA)_2 \cdot 4H_2O$ (**3**) was formed (Figure S4).[8,11]

A detailed examination was performed to further study the solid-state reaction between $Zn(CH_3COO)_2 \cdot 2H_2O$ and HINA in the presence of grinding aids. Figure 2 compares the XRPD patterns of the reaction mixture at different points in reaction time at 80 °C. No obvious change was detected before 45 min. Meanwhile an intermediate phase was formed at 50 min, and the

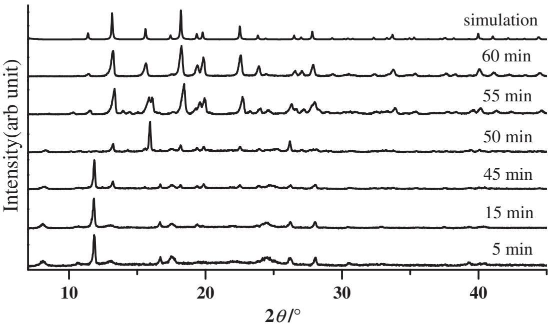
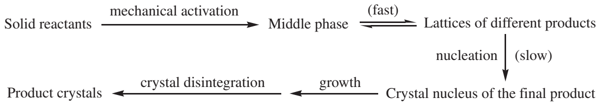


Figure 2. Detailed investigation into the solid-state reaction with grinding aids. The XRPD pattern simulated from the single-crystal data of **2** is shown on the top, and the XRPD patterns of the reactants at different points in reaction time are compared below.

final product **2** was recognized quickly at 55 min after the intermediate phase disappeared. After 60 min the reaction was almost completed.

Solid-state reactions at low-heating temperatures generally undergo several steps according to Kaupp et al.:[9] (a) the phase rebuilding stage where the long-range migrations of reactant molecules take place and an intermediate phase is formed, (b) the phase transformation stage during which the product lattices are fabricated discontinuously, and (c) the crystal disintegration stage. During the first step, reactants are "diffused" into each other and react to form an intermediate phase that is different from the starting one. While in the second step, nucleation must be involved in the formation of product crystals wherein crystal nuclei grow. Based on the reaction process in the case of **2**, the formation of the intermediate phase in the first step is believed to be rate-determining. It took 50 min for the intermediate phase to emerge, and another 5 min for the final product to emerge. Presumably the reactant particles are encapsulated by the long-tailed-grinding-aid molecules, which results in weaker mechanical activation, therefore, the reaction between the two reactants proceeds slower than the reaction does under neat grinding. That in turn allows the formation of the quartz-like structure that possesses higher thermodynamic stability. Of particular interest is that the intermediate phase formed at 50 min is identical to compound **3** (Figure S5[11]).

In sharp contrast, the synthesis under neat grinding is likely kinetic controlled and thus in favor of crystals having advantages on the nucleation rate in the phase transformation stage over any other products. A possible mechanism is proposed in Scheme 2. After the intermediate phase is formed, the lattices of all different products are built fast and reversibly. Since the following nucleation step is slow, the formation of the crystal nuclei of the products becomes the rate-determining step. During the next stages, crystal growth and crystal disintegration are rather fast, so they have no effect on the structure of the final product. Meanwhile, the methanol treatment has an impact on the nucleation step, where the formation of crystal nuclei is accelerated when the solids in the intermediate phase are immersed in methanol. The predominant product nucleates first and grows to furnish the final product crystals. In this regard, product **1** has a higher nucleation rate, and it nucleates prior to any other species in methanol.



Scheme 2. A proposed mechanism for reactions under neat grinding.

It is also noteworthy that the solid-state reactions between $Zn(CH_3COO)_2 \cdot 2H_2O$ and HINA can proceed completely at certain temperatures after a short period of grinding, which suggests that these reactions require low activation energy and they are able to proceed spontaneously after the initial mechanical activation. The grinding increases defects in the crystals that are essential for inducing the solid-state reactions, and the grinding also accelerates homogeneous mixing of the reactants. However, it might not be applicable to other solid-state reactions between metal salts and organic ligands. Similar conclusions were drawn by Pichon et al.[10]

In summary, two known coordination polymers were synthesized through controlled solid-state reactions. Although the nature of the reactions is rather complicated, a rational control can be applied to the solid-state synthesis of coordination polymers. By varying the reaction conditions, the rate-determining step can be rationally adjusted, and consequently different coordination polymers are obtained. Clearly, as a promising preparative approach for coordination polymers toward green chemistry, further investigations need to be resorted to the solid-state reaction synthesis.

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References and Notes

1 B. F. Hoskins, R. Robson, *J. Am. Chem. Soc.* **1990**, *112*, 1546.
2 a) M. Kondo, T. Okubo, A. Asami, S. Noro, T. Yoshitomi, S. Kitagawa, T. Ishii, H. Matsuzaka, K. Seki, *Angew. Chem., Int. Ed.* **1999**, *38*, 140. b) J. Kim, B. Chen, T. M. Reineke, H. Li, M. Eddaoudi, D. B. Moler, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2001**, *123*, 8239.
3 a) B. Moulton, M. J. Zaworotko, *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 117. b) A. U. Czaja, N. Trukhan, U. Müller, *Chem. Soc. Rev.* **2009**, *38*, 1284. c) T. Uemura, N. Yanai, S. Kitagawa, *Chem. Soc. Rev.* **2009**, *38*, 1228.
4 a) A. Stein, S. W. Keller, T. E. Mallouk, *Science* **1993**, *259*, 1558. b) T. Friščić, *J. Mater. Chem.* **2010**, *20*, 7599. c) A. L. Garay, A. Pichon, S. L. James, *Chem. Soc. Rev.* **2007**, *36*, 846.
5 a) J. Yoshida, S. Nishikiori, R. Kuroda, *Chem.—Eur. J.* **2008**, *14*, 10570. b) D. Braga, M. Curzi, A. Johansson, M. Polito, K. Rubini, F. Grepioni, *Angew. Chem., Int. Ed.* **2006**, *45*, 142. c) W. Yuan, T. Friščić, D. Apperley, S. L. James, *Angew. Chem., Int. Ed.* **2010**, *49*, 3916. d) A. Pichon, S. L. James, *CrystEngComm* **2008**, *10*, 1839.
6 O. R. Evans, R.-G. Xiong, Z. Wang, G. K. Wong, W. Lin, *Angew. Chem., Int. Ed.* **1999**, *38*, 536.
7 J. Sun, L. Weng, Y. Zhou, J. Chen, Z. Chen, Z. Liu, D. Zhao, *Angew. Chem., Int. Ed.* **2002**, *41*, 4471.
8 L. C. Yu, H. Liang, C. S. Zhou, Z. F. Chen, *Chin. J. Synth. Chem.* **2005**, *13*, 504.
9 G. Kaupp, *CrystEngComm* **2003**, *5*, 117.
10 A. Pichon, A. Lazuen-Garay, S. L. James, *CrystEngComm* **2006**, *8*, 211.
11 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.