

SYNTHESIS OF ZINC AND CADMIUM GLYCYL-L-PHENYLALANINE COORDINATION POLYMERS: MECHANOCHEMICAL APPROACH

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ABSTRACT

Two-dimensional coordination polymers $[\text{Zn}(\text{Gly-L-Phe})_2]_n$ (**1**) and $[\text{Cd}(\text{Gly-L-Phe})_2]_n$ (**2**) (Gly-L-Phe=glycyl-L-phenylalanine) were mechanochemically synthesized using ball mill. Effects of starting metal salts and presence of added liquid on the reactions were investigated and products were analyzed by infrared spectroscopy and powder diffraction. We have found that reactions proceed surprisingly easily with ZnO and CdO, giving polymers **1** and **2**, respectively. Reactions with hydrated acetates are also facile.

Keywords: mechanochemistry, dipeptide coordination polymers, IR spectroscopy, PXRD.

INTRODUCTION

Mechanochemical reactions are reactions that are induced or initiated by the input of mechanical energy. Mechanochemistry has become increasingly popular in recent years because of its advantages: it can be more efficient, faster and cheaper than classical solution-based processes ^[1]. As opposed to the traditional synthesis, mechanochemistry can be conducted using small or negligible amounts of liquids. Such procedure reduces the cost of the reaction and production of potentially hazardous waste. Also, mechanochemical reactions are usually performed at room temperatures and pressures, thereby consuming less energy. Reactivity and selectivity of mechanochemical reactions can be improved by addition of small amount of liquid (LAG – liquid assisted grinding) and/or ionic salt (ILAG – ion and liquid assisted grinding) ^[2]. These methods broaden possibilities of mechanochemical reactions by enhancing rate of the reaction while directing the reaction to the synthesis of the specific product. Although mechanochemistry is already well-established in the synthesis and processing of various inorganic materials, its use is rapidly growing in the area of organic and coordination chemistry.

Porous coordination polymers or metal organic frameworks (MOFs) have become intensely researched area of materials chemistry. Due to their properties (porosity, low density, high specific surface area and possibility of the design), MOFs could be useful in a wide range of applications, including gases storage, separations and catalysis ^[3]. Coordination polymers and MOFs made of amino acids and peptides as ligands have specific recognition properties and intrinsic chirality that could be useful for some applications, like asymmetric catalysis and enantioselective separation ^[4]. Recently, we have synthesized two-dimensional coordination polymers, $[\text{Zn}(\text{Gly-L-Phe})_2]$ (**1**) and $[\text{Cd}(\text{Gly-L-Phe})_2]$ (**2**) with twofold (4,4) interpenetrated net ^[5]. Such structural feature was observed for the first time in metal-dipeptide frameworks with dipeptides as sole ligands. We have decided to investigate some parameters of mechanochemical synthesis of **1** and **2**: source of metal ions and presence of added grinding

liquid. Our aim is to improve and simplify synthesis by shortening the reaction time, use cheaper reactants, such as metal oxides to reduce amount of the solvent compared to solvothermal synthesis and to improve yield..

EXPERIMENTAL

Materials and methods All chemicals were obtained from commercial vendors and used as received. FT infrared spectra were recorded on Bruker Tensor 37 in the range from 4000 to 400 cm^{-1} . Powder XRD patterns were acquired with APD 2000 diffractometer (Cu $K\alpha$, $\lambda = 1.54056 \text{ \AA}$) in the $5 - 40^\circ 2\theta$ range.

Synthesis Syntheses were performed using Retsch MM 200 ball mill which was operated at 25 Hz. In a typical experiment, 0.15 mmol of metal salt ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, ZnO , $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ or CdO) and 0.30 mmol of dipeptide were loaded into steel or Plexiglass jars along with the stainless steel ball and grinding liquid, where required. Amount of grinding liquid is defined by parameter η ^[6] (ratio of added liquid/sample mass) [$\mu\text{L mg}^{-1}$] and in here it is set at $0.2 \mu\text{L mg}^{-1}$. As grinding liquids, 25wt% solution of ammonia and deionized water were used. Reactions were performed for 60 or 120 minutes and reaction mixture was sampled at 15, 30 and 60 minutes for analysis by IR, while powder XRD data is collected only for the final products.

RESULTS AND DISCUSSION

We have investigated several reaction systems composed of Gly-L-Phe ligand and different zinc and cadmium metal salts with or without added liquid. Grinding of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and Gly-L-Phe with the ammonia solution gives unknown intermediate product after 15 minutes, along with the unreacted dipeptide. Bands present at 3135, 1657, 1178, 1050 cm^{-1} in IR spectra cannot be assigned either to reactants or **1** (Figure 1, left). Infrared spectra of the samples milled for 30, 60 and 120 minutes exhibit new band at 3344 cm^{-1} which can be assigned to the N–H stretching of ammonia. Lack of characteristic bands in IR spectra at 3327, 2967, 1673 and 1153 cm^{-1} clearly shows that **1** is not product of the reaction. Furthermore, in IR spectra of all samples of the system, bands at 2110, 1626, 1338, and 979 cm^{-1} are present and correspond to free dipeptide.

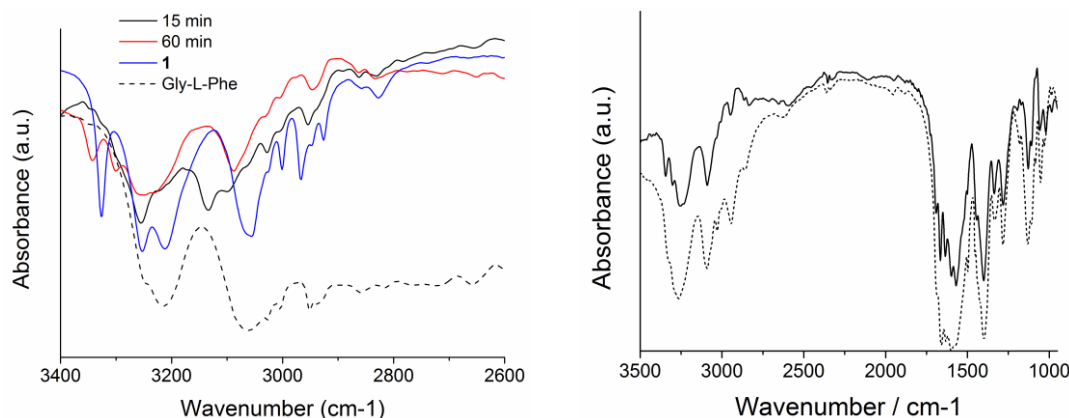


Figure 1. Left: IR spectra of Gly-L-Phe, **1** and products obtained by LAG grinding of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and Gly-L-Phe. Right: IR spectra of products of neat (dashed line) and LAG (solid line) reactions of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and Gly-L-Phe.

When the reaction is performed neat (without added ammonia), IR spectrum of the obtained product is almost the same as the spectrum of the product obtained with LAG (Figure 1, right), except in absence of sharp band at 3344 cm⁻¹. Diffraction patterns of neat and LAG milled samples are shown in Figure 2. It can be seen that grinding with added ammonia affects the reaction, while neat grinding gives poorly crystalline product.

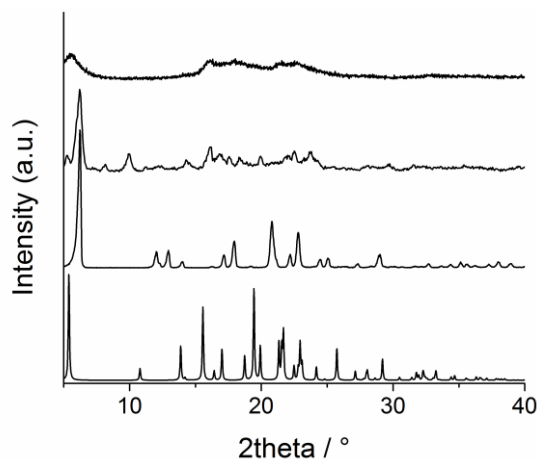


Figure 2. Powder XRD patterns from bottom to top: Gly-L-Phe, **1**, product from LAG grinding Zn(CH₃COO)₂·2H₂O and Gly-L-Phe, product of neat grinding of Zn(CH₃COO)₂·2H₂O and Gly-L-Phe.

When ZnO and Gly-L-Phe are milled without added liquid, no reaction takes place, as expected. However, if the reaction is run with added NH₃ solution, characteristic band in IR spectra (N–H stretching at 3325 cm⁻¹, exactly as in **1**) appears already after 15 minutes (Figure 3, left). Reaction is completed after one hour as confirmed by PXRD analysis, giving less crystalline product than the one obtained by solvothermal reaction (Figure 2, right).

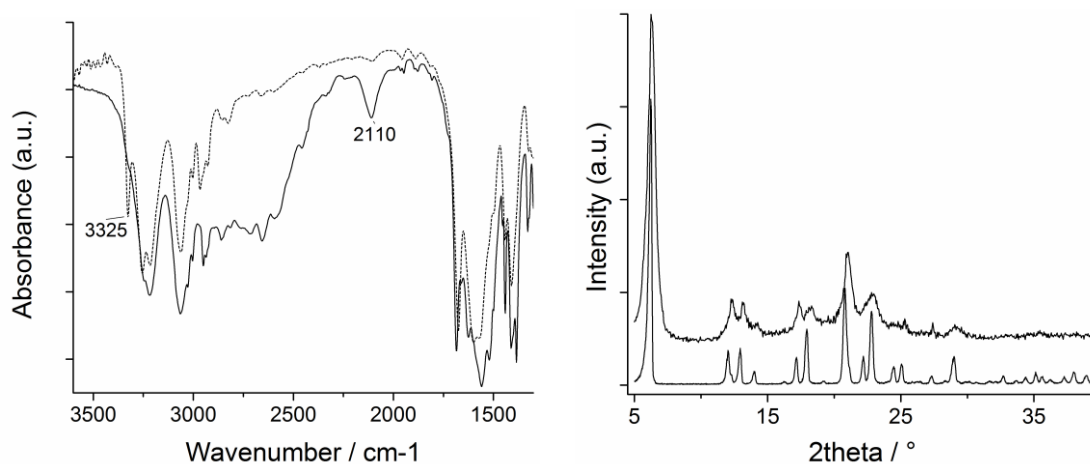


Figure 3. Left: IR spectra of products of neat (solid) and LAG (dashed line) reactions of ZnO and Gly-L-Phe. Right: diffraction patterns of **1** obtained by liquid assisted grinding of ZnO and Gly-L-Phe (top) and solvothermal synthesis (bottom).

Milling of reaction mixture consisting of Cd(CH₃COO)₂·2H₂O and Gly-L-Phe with added NH₃ solution quantitatively gives **2** after 15 minutes. Diffraction pattern shows that the **2** is fully crystalline after one hour of reaction (Figure 4, left, middle pattern). Reaction between CdO and Gly-L-Phe with added NH₃ solution gives **2** after 15 minutes of grinding.

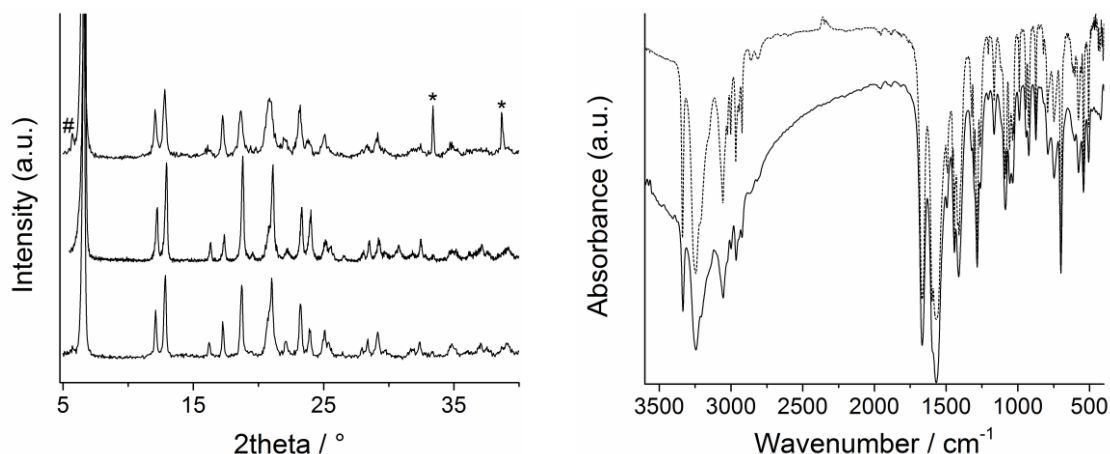


Figure 4. Left: XRD patterns of **2** obtained by: solvothelmal reaction (bottom), LAG reaction of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, Gly-L-Phe and NH_3 solution (middle) and by LAG reaction of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, Gly-L-Phe and H_2O . Diffraction maxima of CdO and Gly-L-Phe are denoted by * and by #, respectively. Right: IR spectra of **2** obtained by: LAG reaction of CdO, Gly-L-Phe and NH_3 solution (dashed line) and solvothelmal reaction (solid line).

Analysis of the IR spectra suggests that the reaction is quantitative, because no bands belonging to free dipeptide were found (Figure 4, right). Also, absence of the red color of the reaction mixture, arising from CdO, confirms that reaction is complete. In accordance with the observation that the reaction with CdO and ammonia proceeds readily, we have decided to use water instead of NH_3 solution. Unexpectedly, after just 15 minutes of the milling, **2** was identified in the IR spectra. Nevertheless, quantitative yield was not achieved after 120 minutes of milling as diffraction maxima of CdO and Gly-L-Phe were present (Figure 4, left, top pattern).

CONCLUSION

Two-dimensional coordination polymers, $[\text{Zn}(\text{Gly-L-Phe})_2]_n$ and $[\text{Cd}(\text{Gly-L-Phe})_2]_n$, were mechanochemically synthesized using ball mill. LAG reaction (NH_3 solution) of Gly-L-Phe with zinc or cadmium oxides completes within 60 minutes. Added NH_3 solution shows the enhancing and accelerating reaction with oxides. Metal acetates behave different: LAG reaction of dipeptide with cadmium acetate gives $[\text{Cd}(\text{Gly-L-Phe})_2]_n$ in 15 minutes of grinding, while reaction with zinc acetate gives unknown product, via unidentified intermediate. In summary, we showed that mechanochemical synthesis of $[\text{Zn}(\text{Gly-L-Phe})_2]_n$ and $[\text{Cd}(\text{Gly-L-Phe})_2]_n$ can be synthesized with different metal salts and with small amount of added liquid, giving crystalline products in shorter time and with increased yield than the solvothelmal method.

REFERENCES

- [1] S. L. James, *et al.*, *Chem. Soc. Rev.* **2012**, *41*, 413–447.
- [2] T. Friščić, *et al.*, *Angew. Chem. Int. Ed.* **2010**, *49*, 712–715.
- [3] F. A. Almeida Paz, *et al.*, *Chem. Soc. Rev.* **2015**, *44*, 6774–6803.
- [4] D. Maspoch, *et al.*, *Chem. Commun.* **2011**, *47*, 7287–7302.
- [5] J. Bronić, *et al.*, *New J. Chem.* **2016**, *40*, 4252–4257.
- [6] T. Friščić, *et al.*, *CrystEngComm* **2009**, *11*, 418–426.