

SYNTHESIS OF ZINC BIS(GLYCLY-L-PHENYLALANINATE) AND ITS CHARACTERIZATION

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ABSTRACT

The solvothermal reaction between Zn^{2+} and glycl-L-phenylalanine was finished giving the crystalline $\text{Zn}(\text{GlyPhe})_2$. A part of the structural as well as thermal properties of the obtained crystals were examined. The characterization was performed using various methods: X-ray powder diffraction, infrared spectroscopy, thermal analysis (TG and DTG), and atomic absorption spectroscopy. Unit cell and its parameters of $\text{Zn}(\text{GlyPhe})_2$ have been determined and reported here.

Keywords: PXRD, dipeptide, IR spectroscopy, TG/DTG.

INTRODUCTION

Metal-organic frameworks (MOFs) are porous crystalline compounds having some interesting features: porosity, low density, high specific surface area. Because of these properties, MOFs could be useful for a wide range of applications, including gases storage, gases separations and catalysis [1,2]. Coordination polymers and MOFs, based on biomolecules, such as amino acids, peptides, nucleobases, carbohydrates and others, have recently attracted a great interest for biological and medical applications [3,4]. Peptides are short chains of amino acids linked by carboxylate-amine ends (-CO-NH-). Depending on amino acid type and sequence, peptides have specific recognition properties and intrinsic chirality that could be useful for some applications, like asymmetric catalysis and enantioselective separation [5]. Due to its chemical and structural properties, peptides show some attractive characteristics as ligands: variety of binding modes, chirality, structural flexibility, hydrogen bonding capabilities and control of side chain, which is relevant to chemical properties. This versatility affords possibility to access numerous functional metal-peptide coordination polymers and MOFs.

EXPERIMENTAL

Synthesis: Dipeptide H-GlyPhe-OH (66.7 mg, 0.3 mmol) was dissolved in 2 mL of aqueous solution of NaOH ($c=0.1 \text{ mol dm}^{-3}$). 1.5 mL of methanolic solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($c=0.1 \text{ mol dm}^{-3}$) was added to dipeptide solution. Reaction mixture was diluted with 4 mL of deionized water and 4.5 mL of methanol. Clear reaction solution was transferred to teflon-lined autoclaves and heated for 72 h at 85 °C. White, micro-crystalline, plate-like product (not suitable for single crystal XRD analysis) was isolated by filtration and washed with small amounts of methanol.

Characterization: Powder XRD data were collected on Phillips PW1820 diffractometer with $\text{Cu K}\alpha$ source. FT-IR spectra were recorded on Bruker TENSOR 37 spectrometer using KBr pellets in transmission mode, in the range from 400 to 4000 cm^{-1} . Thermogravimetric measurements were performed under air, with heating rate of 10 °C min^{-1} using Shimadzu

DTG-60H instrument. Determination of zinc content by atomic absorption spectrometry was carried out on Perkin Elmer AAnalyst 200.

RESULTS AND DISCUSSION

The IR spectra of starting dipeptide (GlyPhe) and crystalline product ($\text{Zn}(\text{GlyPhe})_2$) are shown in Figure 1. In dipeptide IR spectra, broad band from 2200 – 3400 cm^{-1} is assigned to combination of symmetric and asymmetric stretching vibrations of NH_2 , (NH_3^+) group, C–H, and O–H vibrations, including intra- ($\text{N–H}\cdots\text{O}_{\text{amide}}$) and intermolecular ($\text{N–H}\cdots\text{O}_{\text{carboxylate}}$) hydrogen bonds [6]. Upon coordination, band at 2111 cm^{-1} (combination of NH_3^+ deformations) vanished and aforementioned broad band became narrower - indicating deprotonation and coordination through amino group. Doublet at 3254 and 3212 cm^{-1} in $\text{Zn}(\text{GlyPhe})_2$ IR spectra became sharper, and can be assigned to N–H stretching vibration of NH_2 group, which corresponds to symmetric and antisymmetric modes. Sharp peak at 3326 cm^{-1} corresponds to N–H amide stretching vibration, which was not present in free dipeptide due to the hydrogen bonds. C=O amide stretching and N–H bending bands were shifted from 1686 and 1628 cm^{-1} in free dipeptide to the 1672 and 1601 cm^{-1} in $\text{Zn}(\text{GlyPhe})_2$. Carboxylate asymmetric vibration appears at 1570 cm^{-1} , while symmetric vibration could be tentatively assigned as slightly sharper band at 1410 cm^{-1} .

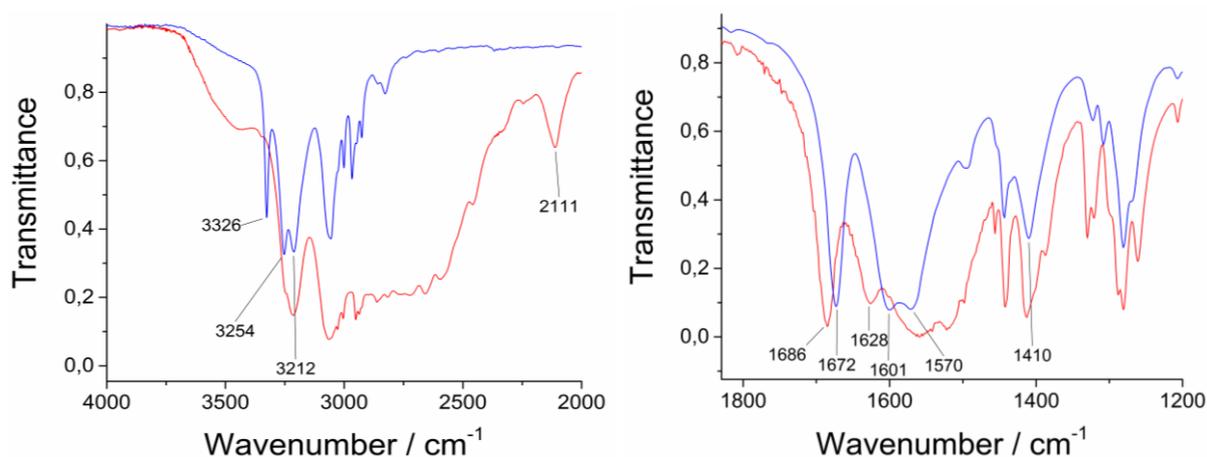


Figure 1. IR spectra of H-GlyPhe-OH (red) and $\text{Zn}(\text{GlyPhe})_2$ (blue) in the two ranges: 4000 – 2000 cm^{-1} (left), and 1800 – 1200 cm^{-1} (right).

Analysis of TG and DTG data (Figure 2) shows that $\text{Zn}(\text{GlyPhe})_2$ is stable up to 300 °C. Afterwards, decomposition of the organic part of the $\text{Zn}(\text{GlyPhe})_2$ lasts up to approximately 500 °C. Two sharp mass loss peaks occur at 347 and 460 °C. Total mass loss of 84% corresponds to the two GlyPhe molecules (theoretical value: 87.2%), while mass residue of 16% gives ZnO molecule.

Zinc content was also determined by flame AAS. Obtained result (12.7%) is in excellent agreement with theoretical value (12.8%) and thermogravimetric analysis (12.9%).

The diffraction pattern was indexed using TOPAS software package [7] and most probable space groups were $C2$, Cm or $C2/m$. Non-centrosymmetric $C2$ space group was selected following the fact that starting dipeptide is pure chiral compound [6b].

The Pawley refinement [8] of the unit cell ($a = 29.4580 \text{ \AA}$, $b = 5.3011 \text{ \AA}$, $c = 7.4989 \text{ \AA}$, $\beta = 95.6024^\circ$) is in good agreement with observed pattern, $R_{wp} = 0.1619$, $R_p = 0.1218$ and shown in Figure 3.

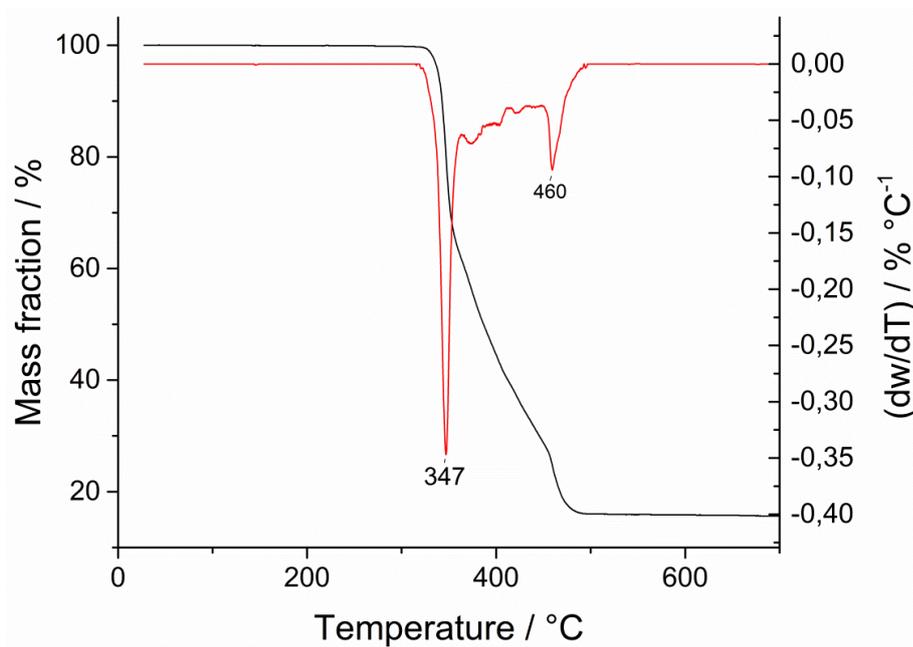


Figure 2. TG and DTG curves of $\text{Zn}(\text{GlyPhe})_2$.

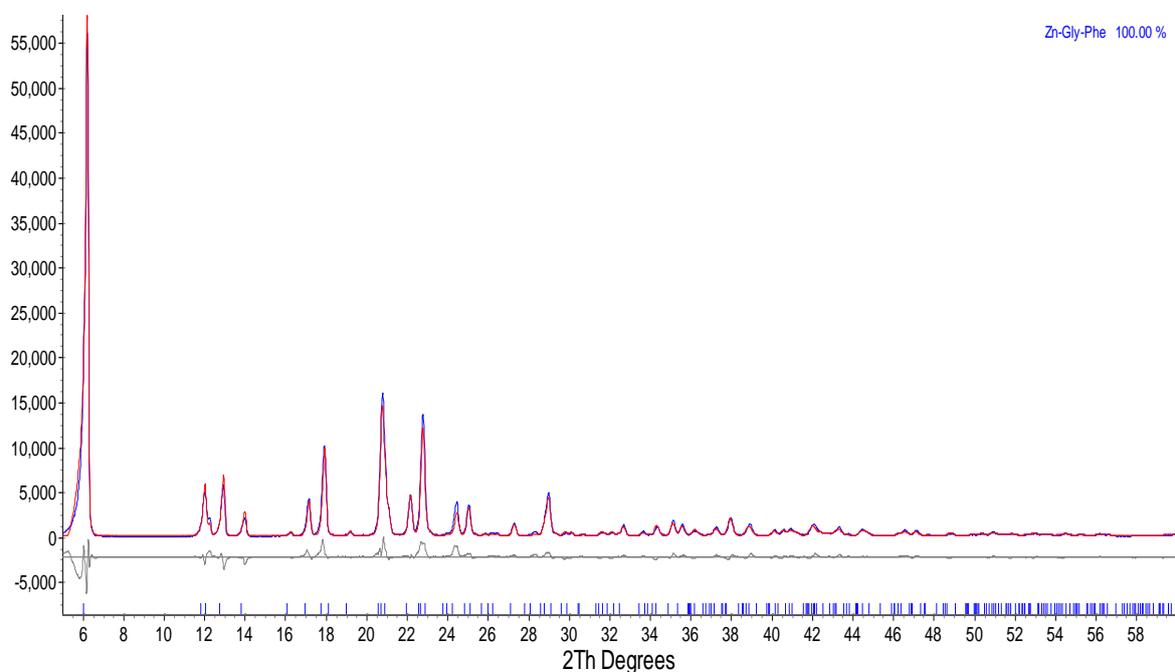


Figure 3. Pawley fit for indexed unit cell. Experimental pattern is blue, calculated pattern is red. Blue tick marks designate calculated peak positions. The difference between calculated and observed patterns is described with grey line.

CONCLUSION

New coordination compound between zinc and glycyl-L-phenylalanine (Zn(GlyPhe)₂) was synthesized solvothermally. It crystallizes in non-centrosymmetric *C2* space group with unit cell dimensions: $a = 29.4580 \text{ \AA}$, $b = 5.3011 \text{ \AA}$, $c = 7.4989 \text{ \AA}$, $\beta = 95.6024^\circ$. Thermogravimetric analysis shows relatively good stability of the Zn(GlyPhe)₂ while the decomposition occurs in range between 300 and 500 °C.

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