One pot synthesis , characterization and mechanism of zinc glycinate monohydrate

HuiFeng^{1, 2,a}, Zhiwei Xu¹, QianfengLi¹, Xiuru Wang¹ and Qiuyue Song¹

¹Heibei DonghuaJiheng Chemical Co. Ltd, Hengshui053000, China

²School of Chemistry & Chemical Engineering, Jiangsu University, Zhenjiang 212013, China

^afenghui0827@163.com

Keywords: zinc glycinate monohydrate, glycine, zinc supplement, bioavailability.

Abstract. A facile method to control the synthesis of zinc glycinate is described. $\text{Zn}(\text{Ac})_2$ and ZnO are used as zinc source, and H^+ is used as catalyst. The composition and structure of the chelate compounds are characterized by infrared spectroscopy (IR), thermogravimetric analysis (TGA) and x-ray powder diffraction (XRD). It proves that the chelate compounds are monoclinic, and meanwhile we discuss the formation mechanism rationally. This is an effective and novel method for the synthesis of high-yield $\text{Zn}(\text{Gly})_2 \cdot \text{H}_2\text{O}$ to realize industrial production.

1. Introduction

In recent years, how to properly use the trace mineral elements to improve its bioavailability is a very interesting but complex topic in the food nutrition and biochemistry. Particularly, Zinc deficiency has become a common phenomenon which will lead to poor immune system, low intelligence, loss of appetite and so on. As we all know, direct zinc supplement is not only bad absorption, but also will bring to negative effect [1-3]. Therefore, we need to find a dual role of zinc supplement nutritious and therapeutic to address the problem.

Compared with traditional zinc complement zinc sulfate (ZnSO_4) and zinc gluconate ($\text{Zn}(\text{C}_6\text{H}_{11}\text{O}_7)_2$), zinc glycinate is a good candidate for it. The content of the zinc is 30.28% in the pure zinc glycinate. Up to now, it is one of the highest zinc supplement reagent, many scholars at home and abroad have been studying the synthesis and structure of $\text{Zn}(\text{Gly})_2$ at different levels [4-6]. Taken together, the synthesis of $\text{Zn}(\text{Gly})_2$ has aqueous synthesis method, solid-phase synthesis method, electrolytic method and phase equilibrium method [4,5]. The zinc source comes from Zn , ZnCl_2 , ZnSO_4 and ZnCO_3 , etc. Although the analysis of structures of the zinc glycinate has been reported, there is not a systematic analysis and research. In this paper, we demonstrate the synthesis of $\text{Zn}(\text{Gly})_2$ via one pot chemistry method using $\text{Zn}(\text{Ac})_2$ and ZnO as zinc source. $\text{Zn}(\text{Ac})_2$ is used as promotion reagent of ZnO and catalyst to the formation of the $\text{Zn}(\text{Gly})_2$. The as-prepared crystal has been investigated by various characterization techniques and its formation mechanism is rationally discussed.

2. Experimental section

Sample Preparation. The reagents in this work, including zinc acetate dehydrate ($\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$), zinc oxide (ZnO), and ethanol (EtOH) were of analytical grade from the Tianjin Damao Chemical Factory of China, the glycine and distilled water came from Heibei DonghuaJiheng Chemical Co. Ltd. All chemicals were used as received without further purification.

In a typical synthesis, 20g glycine (0.267mol), 9.04g ZnO (0.111mol) and 4.88g $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ (0.022mol) were added to distilled water (60ml) in a two-necked flask. Under stirring, it was heated to 90 °C in an oil bath and maintained at this temperature for 120 min. Then the product was obtained by vacuum filtration, washed with ethanol several times, and dried at 30 °C.

Characterization. Powder X-ray diffraction (XRD) patterns of the samples were collected on a D8 Advance diffractometer (Bruker, German) with graphite-monochromatized $\text{Cu K}\alpha$ radiation ($\lambda =$

1.54178Å). Infrared spectra were recorded on a Nicolet iS50 fourier transform spectrometer between 400 and 4000 cm^{-1} . Thermogravimetric analysis(TGA) was carried out on a Netzsch STA 449C analyzer in the protection of N_2 between 25 and 400 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C min}^{-1}$.

2. Results and discussion

In the present work, we only use the H^+ as promoting solvent and catalyst, ZnO as zinc source in the synthesis process. However, the introduction of the trace H^+ fail in dissolving theundissolved ZnO , and meanwhile the product is not easy to separation. Even if hot separation and crystallization, the yield of product is only about 20%.In order to address the knotty problem, it is necessary to seek for a proper synthetic tactic. Very recently, our group developed a convenient strategy to synthesize $\text{Zn}(\text{Gly})_2$.The addition of $\text{Zn}(\text{Ac})_2$ can completely dissolve the ZnO at a certain condition, and it is easy to obtain the target products through separation at ambient temperature. Ifwe add the $\text{Zn}(\text{Ac})_2$ without ZnO , the reaction result in forming lots of HAc so that the product can't be crystalized, precipitated and separated. In our synthesis strategy, the yield of the $\text{Zn}(\text{Gly})_2$ is 54.85% at first time, then adding the same amount of reactant to the first filtrated liquid to further reaction, we can get 98.92% $\text{Zn}(\text{Gly})_2$. At the third time, the yield of the product is 98.72%. We are believing that the reaction system has been designed by our group based on this idea(eqn (1,2)).

Fig. 1 shows the X-ray diffraction (XRD) pattern of the Gly and as-prepared $\text{Zn}(\text{Gly})_2$. The diffraction peaks(Fig. 1a) at 2θ 14.9°, 19.0°, 23.9°and 36.6°match well with the characteristic peaks of monoclinic glycine (α -gly)[9,13].However, The main diffraction peaks (Fig.1b) of the zinc glycinate obviously occur to displacement,and the interplanar spacing (d) and relative intensity are also changed. It indicates that the chelating effect of glycine and zinc, rather than the simple mixture of glycine and zinc . The diffraction peaks of the obtained zinc glycinate high and sharp indicate that the crystal structure is fine ,and the zinc glycinate is confirmed as triclinic or pseudo-momoclinic[5].

Fig. 1The XRD patterns of (a)the glycine and (b) zinc glycinate

Fourier Transform infrared spectroscopy (FTIR) is used to examine the product obtained from the typical synthetic procedure[10-12]. As shown in Fig.2a ,the glycine have a broad absorption from 3100 cm^{-1} to 2400 cm^{-1} , the weak band at about 3151 cm^{-1} is assigned to the antisymmetric stretching of the NH_3^+ group.while the $\text{Zn}(\text{Gly})_2$ appear a sharp bands from 3400 cm^{-1} to 3100 cm^{-1} ,and the band of NH splits andshifts to higher frequencies at 3299.56 cm^{-1} and 3263.58 cm^{-1} after the formation of complexes, which are corresponding to the ν_{as} and ν of NH bond, and meanwhilethe asymmetric

bending and symmetric bending of NH_3^+ have also changed. In the Fig.2b, We can clearly see the stretching vibration peak of Zn-O bond at 489cm^{-1} [8], This further shows that the carboxyl group participated in coordination. Interestingly, we also observe stretching vibration peak of Zn-N bond at about 598cm^{-1} [7],and the peak of O-H(1574.29cm^{-1}) affords an accessorial proof for existence of crystal water.

Fig. 2 The IR spectra of (a)the glycine and (b) zinc glycinate

TGA analyses are properly performed to examine the content of crystall water. As displayed in Fig.3, the $\text{Zn}(\text{Gly})_2$ show an obvious weight loss in TGA heating process. 7.75% weight loss is measured for the as-prepared product. The weight loss can be attributed to the desorption of crystall water, and the weight loss date is consistent with the theoretical calculation value of only one crystall water, therefore the real structure is $\text{Zn}(\text{Gly})_2 \cdot \text{H}_2\text{O}$.

Fig. 3 The TG analysis of the $\text{Zn}(\text{Gly})_2$

4. Conclusions

In summary, The above investigations show that the route is an effective method for the synthesis of $\text{Zn}(\text{Gly})_2 \cdot \text{H}_2\text{O}$ by one pot chemistry method using $\text{Zn}(\text{Ac})_2$ and ZnO as zinc source, and H^+ is used as catalyst, then discuss the formation mechanism rationally. This work provides an alternative route

for synthesizing metal chelates of glycine. We believe that this method is simple, inexpensive and easy to operation and will be helpful for industrial production.

Acknowledgements.

This work was financially supported by Hebei Donghua Jiheng Chemical Co. Ltd, thanks to Yongquan Yang for help in test.

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