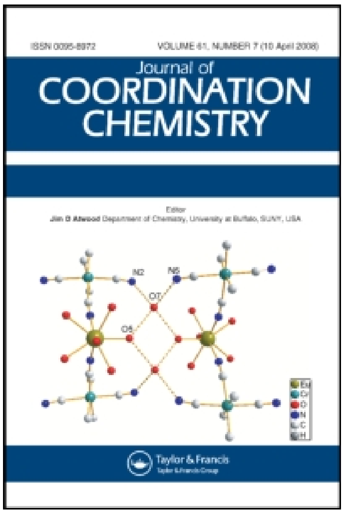

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Synthesis of metal-organic frameworks from the system metal/L-glutamic acid/TEA/H_2O

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Three metal-organic frameworks (MOFs) with similar zeolite-like 3-D structures, Zn(L-Glu)(H_2O) · H_2O, Cu(L-Glu)(H_2O) · H_2O, and Co(L-Glu)(H_2O) · H_2O, have been obtained from metal/L-glutamic acid/TEA/H_2O systems, whereby the weak base triethylamine (TEA), rather than the more typically used NaOH or Na_2CO_3, has been used to adjust the pH of the solution. A systematic and detailed exploration of the synthesis conditions has revealed that not all transition metals may be coordinated to L-glutamic acid and that the range of conditions under which the three MOFs remained stable was different. The metal/L-glutamic acid/TEA/H_2O system offers an effective means of obtaining MOFs.

Keywords: Metal–organic frameworks; L-Glutamic acid; Triethylamine; Synthesis

1. Introduction

Metal-organic frameworks (MOFs) are a new class of materials built up by linking metals with various organic ligands through strong bonds [1]; some show applications in catalysis [2], adsorption [3], magnetism [4], nonlinear optical activity [5], and many other fields [6]. The metals are usually derived from transition metals and their oxides. The bridging ligands are typically cyanide, pyridine, phosphate, and carboxylate [7]; amino acids, which are ubiquitous ligands in biology as well as being the basic building units of proteins, have two or more types of coordination atoms and can act as bridging ligands [8]. However, the main focus of the extensive studies on amino acid coordination chemistry has been on their biologically relevant complexes. Work on amino acids as bridging ligands is still in its infancy [9–11].

L-Glutamic acid is an acidic amino acid with one amine and two carboxylic acid groups. Each of these functional groups is capable of binding to metal centers and glutamate has a variety of coordination modes. This polyfunctionality makes it a potential organic node for the construction of MOF materials. As early as 1966, Gramaccioli obtained complexes of Cu and Zn with glutamate ($CuC_5H_7NO_4 \cdot 2H_2O$, $ZnC_5H_7NO_4 \cdot 2H_2O$) by evaporation of the volatiles from mixtures of the metal salts with glutamic acid [12, 13]. The crystal structures were also determined. In 1998,

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Mizutani *et al.* [14] prepared $[Cu(L\text{-}/D\text{-}Glu)(H_2O)]\cdot H_2O$ by slow evaporation of water from an aqueous solution containing L-/D-Glu and $Cu(ClO_4)_2\cdot 6H_2O$ with the pH adjusted by K_2CO_3, and discussed the structure from the viewpoint of self-assembly. More recently, Zhang *et al.* [15] demonstrated that glutamate, as a multidentate ligand, could be used for assembly of zeolite-like 3-D networks of $Co(L\text{-}Glu)(H_2O)\cdot H_2O$.

After the pioneering work concerned with material structures, we sought to explore the possibility of generating MOFs between metals and L-glutamic acid under hydrothermal conditions. In contrast to the previously used evaporation method, we employed a modified procedure, namely a metal/L-glutamic acid/TEA/H_2O (TEA = triethylamine) system, in which the weak base TEA, rather than NaOH or Na_2CO_3, was used to adjust the pH of the solution. In this way, three materials with similar zeolite-like 3-D structures, $Zn(L\text{-}Glu)(H_2O)\cdot H_2O$, $Cu(L\text{-}Glu)(H_2O)\cdot H_2O$ and $Co(L\text{-}Glu)(H_2O)\cdot H_2O$, were obtained. This manuscript describes recent work in our laboratory on the synthesis of Zn^{2+}-, Cu^{2+}-, and Co^{2+}-based structures with L-glutamic acid under different hydrothermal conditions. XRD, SEM, and FT-IR have been employed to characterize the synthesized samples.

2. Experimental

2.1. *Starting materials*

Silver nitrate ($AgNO_3$, 99.9%, Tianjin Le Tai Chemical Supermarket), zinc nitrate ($Zn(NO_3)_2\cdot 6H_2O$, 99.0%, The Third Company of Tianjin Chemical Reagents), copper nitrate ($Cu(NO_3)_2\cdot 3H_2O$, 99.5%, Tianjin Kermel Chemical Reagents Development Center), cobalt chloride hexahydrate ($CoCl_2\cdot 6H_2O$, 99.0%, The Third Company of Tianjin Chemical Reagents), nickel chloride ($NiCl_2\cdot 6H_2O$, 98%, Tianjing Dengfeng Chemical Reagents Company), chromium(III) nitrate ($Cr(NO_3)_3\cdot 9H_2O$, 99.0%, Sinopharm Chemical Reagent Co., Ltd.), and triethylamine (TEA, 99.0%, Tianjing Fangde Tech Co., Ltd.) were A.R. grade reagents. L-Glutamic acid ($C_5H_9NO_4$, 98.5%, Beijing Aoboxing Biotech Company Ltd.) was a B.R. grade reagent. All chemicals were used without purification. Distilled water was prepared in our laboratory.

2.2. *Synthesis*

Triethylamine was added to an aqueous solution containing L-glutamate and the appropriate metal salt, and the mixture was heated in a Teflon-lined autoclave at 100°C for three days to prepare the L-glutamate complex. The resulting products were washed with distilled water and dried in air.

2.3. *Characterization*

Powder XRD patterns of dried samples were recorded on a Rigaku D/Max 2500 powder X-ray diffraction apparatus using Cu-Kα1 radiation and operating at 40 kV and 100 mA. The morphologies of the materials were observed by a JSM-6700F scanning electron microscope. The samples were coated with gold in order to increase their conductivity before scanning. IR spectra were recorded on an FT-IR8400 spectrometer in the range 4500–400 cm^{-1}. The samples were dried for 30 min under an infrared lamp prior to their incorporation into KBr discs.

3. Results and discussion

3.1. *Synthesis*

3.1.1. The influence of different metals. In exploratory experiments, several transition metal salts were employed as starting materials. From table 1, it can be seen that successful hydrothermal syntheses were accomplished with Zn^{2+}, Cu^{2+} and Co^{2+}; $AgNO_3$, $NiCl_2 \cdot 6H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$ yielded only amorphous solids. Consequently, not all transition metals can be coordinated to L-glutamic acid under hydrothermal conditions.

3.1.2. The influence of TEA. The pH is a very important parameter for formation of metal–amino acid assemblies as the amine and the carboxylic acid coexist in the same system. In some cases, different pH values can generate compounds of completely different form [8, 10]. In the present work, we adopted the weak-base TEA instead of the more typically used NaOH or Na_2CO_3 to adjust the pH of the solution in our amino acid system. The results are summarized in tables 2–4 of Supplementary Material.

When other conditions are fixed, appropriate TEA content is essential for formation of product. Zn(L-Glu)$(H_2O) \cdot H_2O$ is produced over a broad range of TEA :: $Zn(NO_3)_2 \cdot 6H_2O$ ratios, from 3 : 2 to 5 : 2. Cu(L-Glu)$(H_2O) \cdot H_2O$ is produced over a range from 3 : 2 to 7 : 4. Co(L-Glu)$(H_2O) \cdot H_2O$, on the other hand, requires a ratio of TEA : $CoCl_2 \cdot 6H_2O$ close to 2 : 1.

3.1.3. The influence of L-glutamate/metal salts. Different molar ratios of L-glutamate to metal salt may influence the nature of the resulting products (tables 5–7 of Supplementary Material). The results indicate that changing the molar ratio of L-glutamate to metal salt in the present system does not result in new coordination patterns under hydrothermal conditions.

3.1.4. The influence of H_2O content. The H_2O content represents the concentration of the precursor, which usually influences crystal growth. Cu(L-Glu)$(H_2O) \cdot H_2O$ and

Table 1. The influence of different metals.

Composition of reaction				Phase
$AgNO_3$	L-Glutamic acid	H_2O	TEA	Amorphous solid
$Zn(NO_3)_2 \cdot 6H_2O$	L-Glutamic acid	H_2O	TEA	Zn(L-Glu)$(H_2O) \cdot H_2O$
$Cu(NO_3)_2 \cdot 3H_2O$	L-Glutamic acid	H_2O	TEA	Cu(L-Glu)$(H_2O) \cdot H_2O$
$CoCl_2 \cdot 6H_2O$	L-Glutamic acid	H_2O	TEA	Co(L-Glu)$(H_2O) \cdot H_2O$
$NiCl_2 \cdot 6H_2O$	L-Glutamic acid	H_2O	TEA	Amorphous solid
$Cr(NO_3)_3 \cdot 9H_2O$	L-Glutamic acid	H_2O	TEA	Amorphous solid

Co(L-Glu)(H_2O) · H_2O are very sensitive to H_2O content, but Zn(L-Glu)(H_2O) · H_2O is not (tables 8–10 of Supplementary Material).

The effects of some other synthesis conditions on the formation of MOFs in the metal/L-glutamic acid/TEA/H_2O system were investigated. Though the three materials could all be obtained under similar conditions, Zn(L-Glu)(H_2O) · H_2O was stable over a wide range of conditions, but Cu(L-Glu)(H_2O) · H_2O and Co(L-Glu)(H_2O) · H_2O proved to be rather sensitive to the conditions, and a small change resulted in appearance of amorphous solids. The hydrothermal conditions in the metal/L-glutamic acid/TEA/H_2O system offers an effective means of obtaining MOFs.

3.2. *Characterization*

3.2.1. SEM analysis of the three materials. The three samples that we obtained were all crystalline, Zn(L-Glu)(H_2O) · H_2O as white crystals, Cu(L-Glu)(H_2O) · H_2O as light-blue crystals and Co(L-Glu)(H_2O) · H_2O as purple-red crystals. SEM images (see figures 1–3 of Supplemental Material) show that Zn(L-Glu)(H_2O) · H_2O is prismatic and more regular than Cu(L-Glu)(H_2O) · H_2O or Co(L-Glu)(H_2O) · H_2O.

3.2.2. XRD patterns of the three materials. XRD patterns of the three materials are provided in figure 4 of Supplemental Material. The relative diffraction intensities and peak positions for Zn(L-Glu)(H_2O) · H_2O [figure 4(a) of Supplemental Material] and Cu(L-Glu)(H_2O) · H_2O [figure 4(b) of Supplemental Material] corresponded to the diffraction data of zinc glutamate dehydrate and copper glutamate dehydrate according to the available JCPDS cards [21-1981] and [21-1599]. Moreover, the relative diffraction intensities and peak positions of the Co(L-Glu)(H_2O) · H_2O sample were identical to those of Co(L-Glu)(H_2O) · H_2O reported in the literature [15]. The main peak positions and relative crystallinities of the three samples were quite similar. According to structure analyses in the literature [12, 13, 15], they are all similar complexes.

3.2.3. IR spectra of the three materials. IR spectra of the compounds feature asymmetric and symmetric absorptions of the carboxylate groups at 1556 and 1408 cm^{-1} for Zn(L-Glu)(H_2O) · H_2O, at 1571 and 1408 cm^{-1} for Cu(L-Glu)(H_2O) · H_2O, and at 1542 and 1415 cm^{-1} for Co(L-Glu)(H_2O) · H_2O, indicating that the carboxylate groups are coordinated. The appearance of two absorption bands at 3249 and 3334 cm^{-1} for Zn(L-Glu)(H_2O) · H_2O, at 3221 and 3319 cm^{-1} for Cu(L-Glu) (H_2O) · H_2O, and at 3249 and 3334 cm^{-1} for Co(L-Glu)(H_2O) · H_2O may be attributed to N–H stretching modes, suggesting that the amino N atom is also coordinated to the metal ion.

4. Conclusion

In summary, three MOFs with similar zeolite-like 3-D structures, Zn(L-Glu)(H_2O) · H_2O, Cu(L-Glu)(H_2O) · H_2O, and Co(L-Glu)(H_2O) · H_2O, have been obtained from the metal/L-glutamic acid/TEA/H_2O system in a method that differs from the previous solvent evaporation method. Moreover, a systematic and detailed exploration of the synthesis conditions has shown that not all transition metals may be coordinated to L-glutamic acid, and that the ranges of conditions over which the three MOFs remained stable were different. Zn(L-Glu)(H_2O) · H_2O was stable over a wide range of conditions, but Cu(L-Glu)(H_2O) · H_2O and Co(L-Glu)(H_2O) · H_2O proved to be quite sensitive to changes in the conditions. The metal/L-glutamic acid/TEA/H_2O system has demonstrated potential for obtaining MOFs.

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