SYNTHESIS AND CHARACTERIZATION OF A NEW Cd(II)-GLYCYLGLYCINE COMPLEX. AQUEOUS Cd(II)-GLYCYLGLYCINE SPECIATION STUDIES

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Abstract

Amino acids and peptides are among the most common biomolecules and they are considered as effective metal binding sites under physiological conditions. Cadmium belongs to a category of heavy metal ions (cadmium, mercury, lead) that have increasingly attracted research attention over the years, due to their toxic manifestations in the environment and various organisms, including plants and humans. The scope of this research is to probe and synthetically study the aqueous Cd(II)-glycylglycine speciation relevant to Cd(II) toxicity.

Keywords: cadmium, glycylglycine, aqueous speciation.

Introduction

As a toxic metal ion, Cd(II) is absorbed by the liver, ultimately finding its way to the kidney, the critical organ from the toxicity point of view (Bevan, 1989). The exact mechanisms by which cadmium toxicity arises, however multifaceted, remains unknown. Oligopeptides are normal constituents of intracellular and extracellular fluids of humans and animals, e.g., as encephalins, glutathione, carnosine, and anserine. Furthermore, oligopeptides, particularly dipeptides, may enter the bloodstream during protein absorption or parenteral nutrition (Prockopp, 1962; Adibi, 1971; Steinhardt, 1984). In this study, we investigated the ability of the simplest dipeptide glycylglycine to promote aqueous chemical reactivity with Cd(II) as a first step toward modelling of the bonding modes of peptides to toxic metal ions.
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Experimental

The synthesis of $[\text{Cd}(\text{H}_2\text{NCH}_2\text{CONHCH}_2\text{COO})_2] \cdot 2\text{H}_2\text{O}$ was carried out under hydrothermal conditions in aqueous media (nanopure water), where the pH was adjusted with NaOH solution at 7.5~8.0. The stoichiometric reaction for the synthesis of the new complex of Cd(II) with glycylglycine is given in figure 1.

$$\text{Cd(NO}_3\text{)}_2 + 3 \text{H}_2\text{NCH}_2\text{CONHCH}_2\text{COOH} + \text{NaOH} \rightarrow [\text{Cd}(\text{H}_2\text{NCH}_2\text{CONHCH}_2\text{COO})_2] \cdot 2\text{H}_2\text{O}$$

Fig. 1. Reaction of the synthesis of $[\text{Cd}(\text{H}_2\text{NCH}_2\text{CONHCH}_2\text{COO})_2] \cdot 2\text{H}_2\text{O}$ complex

The crystalline product was isolated and characterized spectroscopically and structurally by the following techniques: FT-Infrared (Figure 2), X-Ray Crystallography (Figure 3).

Fig. 2. FT-IR spectrum of complex $[\text{Cd}(\text{H}_2\text{NCH}_2\text{CONHCH}_2\text{COO})_2] \cdot 2\text{H}_2\text{O}$
The speciation studies were carried out by potentiometric triturations of the ligand glycylglycine alone, and Cd(II) with glycylglycine in various metal ion to ligand molar ratios. The titration curves were evaluated by two different potential speciation models.

Conclusions

In the course of the herein presented research, the ability of glycylglycine dipeptide to promote complexation chemistry with Cd(II) was examined. Our studies were carried out in aqueous media under hydrothermal conditions. Cadmium reacted with glycylglycine in aqueous solution, at pH~8, and led to the formation of [Cd(H₂NCH₂CONHCH₂COO)₂]·2H₂O complex. The product was isolated in a crystalline form and was characterized structurally and spectroscopically. The speciation studies a) emphasize the plethora of species present in the aqueous distribution of the binary Cd(II)-glygly system, and b) point out the structural features of the arisen aqueous...
species that resemble those encountered in the solid state structure of the synthesized and isolated complex 1. Collectively, the physicochemical features of species in the 6.5-9.0 pH region of the speciation diagram derived from the potentiometric studies, hints to the complexity of the requisite speciation and significance of the synthetic approach of pH-dependent synthesis in delineating the fundamental aspects of the toxic Cd(II) (bio)chemistry with low molecular mass physiological biological targets in cellular media.

Chemical reactivity experiments and biological studies to determine the toxicity of compounds such as 1, is one of the basic targets of our research, and are currently ongoing in our lab.

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References


