

Structural speciation in the binary systems of Cd(II) with hydroxycarboxylate substrates

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Abstract

Cadmium is a formidable environmental metallotoxin. The involvement of Cd(II) in cellular pathologies in lower and higher organisms entails interactions with both low and high molecular mass targets. Hydroxycarboxylate substrates are such low molecular mass key cellular molecules contributing to cellular physiology. They are excellent metal ionic chelators promoting complex formation and metal ion absorption by biological tissues. Poised to comprehend Cd(II) toxicity at the molecular level, the aqueous synthetic chemistry of that metal ion with hydroxycarboxylic acids was investigated in aqueous media.

Keywords: Cd(II)-hydroxy-carboxylate interactions, citric acid, ahydroxy-carboxylic acid.

Introduction

Heavy metal ions have been known for their direct and indirect influence on the pathology of a number of human, animal and plant diseases. Among them outstanding are the following: cadmium, nickel, mercury, lead, etc. In all cases of metallotoxin-linked diseasecausing effects, there exist a myriad of mechanisms operating at the molecular level. Factors affecting such mechanisms are uniquely associated with the nature and chemical reactivity of the heavy metal ion in question. Therefore, key to understanding the molecular toxicity of heavy metallotoxins and subsequently developing the appropriate diagnostic, detective and remediation technologies is delineating the interactions of these metallotoxins with low and high molecular mass cellular targets. In this sense, our lab has developed methodologies to identify, synthesize, isolate and characterize such species (in the solid state and in solution) arising through binary interactions of one of the toxic metal

ions, i.e. Cd(II) [1] with (hydroxyl)-carboxylate substrates inherent to cellular physiology [2].

Experimental

The synthesis of various complexes was achieved expediently by reacting cadmium nitrate and citric acid in water. The chemical reactivity was in line with the existing aqueous speciation studies and the pH-dependence nature of the interactions developing between Cd(II) and hydroxyl carboxylate species. The use of base in the synthesis reaction mixture was important in the adjustment of the pH of the solutions to appropriate values and concurrently essential for the provision of the necessary counter ions for the subsequently derived anionic complexes (where applicable). The resulting colorless solutions were treated with ethanol at 4 °C and afforded efficiently colorless crystalline materials. Representative stoichiometric reactions leading to binary complexes of Cd(II) with citric acid are shown schematically below (Figure 1):

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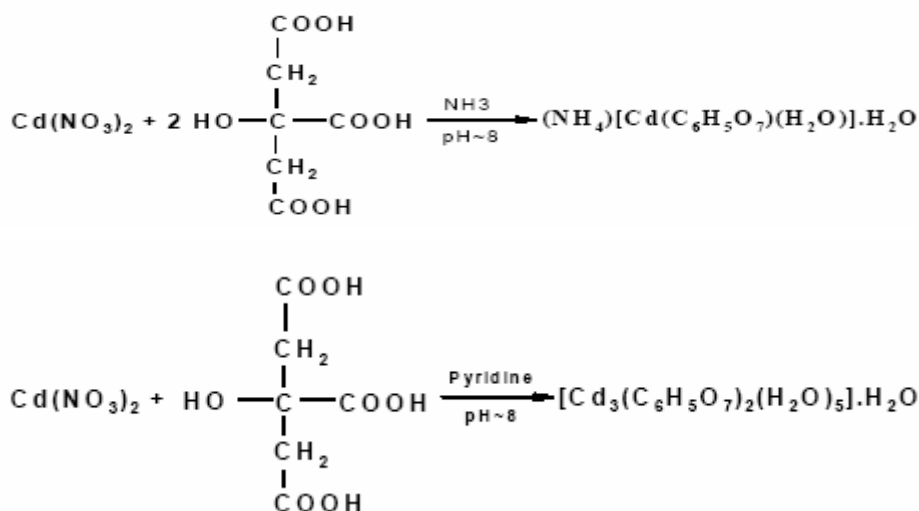


Figure 1. Reactions for the syntheses of $(\text{NH}_4)[\text{Cd}(\text{C}_6\text{H}_5\text{O}_7)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ and $[\text{Cd}_3(\text{C}_6\text{H}_5\text{O}_7)_2(\text{H}_2\text{O})_5] \cdot \text{H}_2\text{O}$ complex

The crystalline products were isolated and characterized analytically, spectroscopically and structurally by the following

techniques: FTInfrared (Figure 2), X-Ray crystallography and ^{13}C -, ^{113}Cd -MAS NMR.

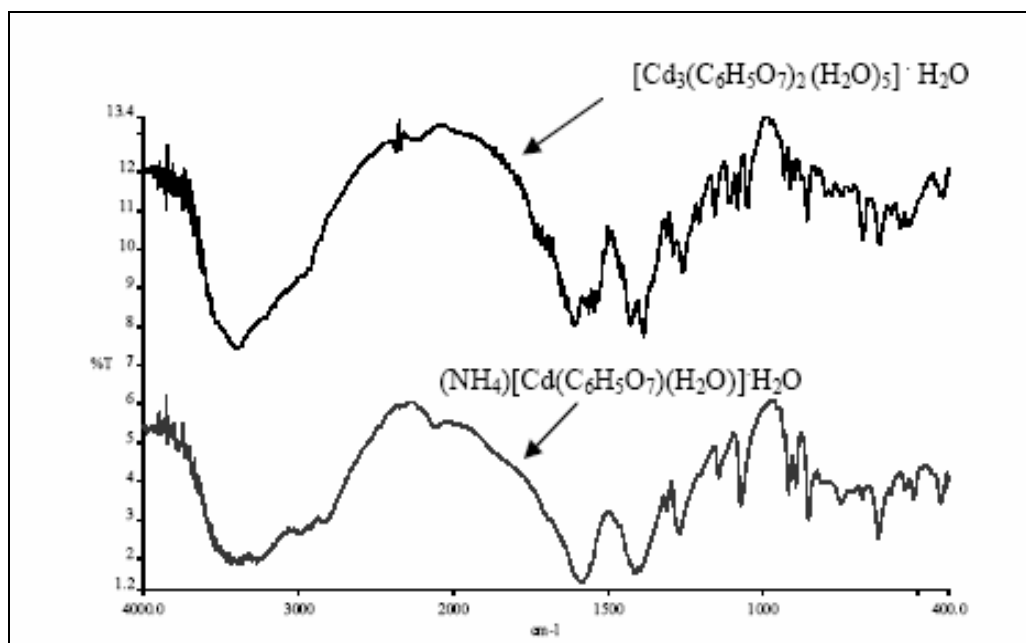


Figure 2. FT-IR spectra of complexes $(\text{NH}_4)[\text{Cd}(\text{C}_6\text{H}_5\text{O}_7)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ and $[\text{Cd}_3(\text{C}_6\text{H}_5\text{O}_7)_2(\text{H}_2\text{O})_5] \cdot \text{H}_2\text{O}$

Analogous synthetic chemistry was carried out with α -hydroxyisobutyric acid and methyl lactic acid.

Conclusions

The results of this study support a diverse and complex chemical reactivity in the selected binary Cd(II)-(O-containing) substrate systems, consistent with the requisite aqueous speciation distribution investigated and known so far. Cadmium reacted with citric acid in aqueous solution, at pH~3, and afforded complex $[\text{Cd}_3(\text{C}_6\text{H}_5\text{O}_7)_2(\text{H}_2\text{O})_5] \cdot \text{H}_2\text{O}$ while at pH~8 afforded the mononuclear complex $(\text{NH}_4)[\text{Cd}(\text{C}_6\text{H}_5\text{O}_7)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ [3]. The collective physicochemical properties of such species bearing citrate [4] provide ample information on the nature of Cd(II)-(O-containing) substrate interactions involved, thereby shedding light on analogous processes at the cellular level and projecting details that might be useful in the development of advanced materials technologies.

Chemical reactivity studies involving binary and ternary Cd(II) systems with O-containing substrates of variable nature and structure, are currently ongoing.

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