

SYNTHESIS AND CHARACTERIZATION OF NEW CD(II)- CITRATE COMPLEXES. AQUEOUS CD(II)-CITRATE SPECIATION STUDIES

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Abstract

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 the various organisms living in it, including plants and humans. Citric acid is an excellent chelator in several interaction systems with metal ions, resulting in the formation of several complexes. The scope of this research is to probe and synthetically study the aqueous Cd(II)-citrate speciation relevant to Cd(II) toxicity.

Key words: *cadmium, citric acid, citrate complex.*

Introduction

As a toxic metal, 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. Of the physiological metal ion binders capable of promoting aqueous interactions with Cd(II) (an essential factor (Hue, 1986; Matzapetakis, 1998) in the aqueous media) the tricarboxylic citric acid appears to be a very prevalent ligand (Glusker, 1980; Martin, 1986). The presence of citric acid in many biological systems as well as its interactive linkage with several metal ions, including Cd(II), has prompted us to study in depth the interactions of Cd(II) with citrate in the physiological pH range.

Experimental

The synthesis 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 $[\text{Cd}_3(\text{C}_6\text{H}_5\text{O}_7)_2(\text{H}_2\text{O})_5]\cdot\text{H}_2\text{O}$ took place in the open air and in aqueous media (nanopure water), under specific pH (NH_3 and pyridine, respectively were used to raise the pH of the respective reaction medium) and temperature conditions. The stoichiometric reactions for the syntheses of complexes of Cd(II) with citric acid are given in figure 1.

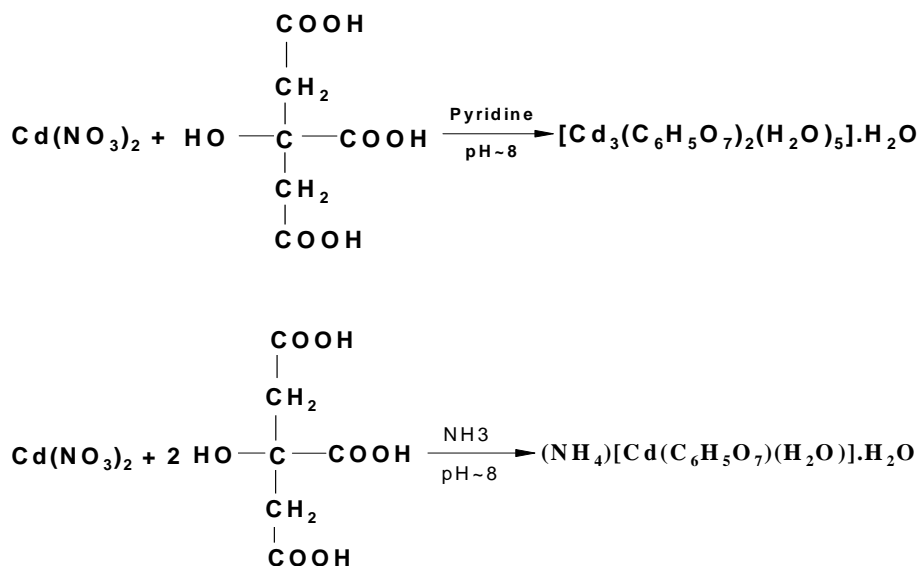


Fig. 1. Reactions for the syntheses of $(\text{NH}_4)[\text{Cd}(\text{C}_6\text{H}_5\text{O}_7)(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ and $[\text{Cd}_3(\text{C}_6\text{H}_5\text{O}_7)_2(\text{H}_2\text{O})_5]\cdot\text{H}_2\text{O}$ complex

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

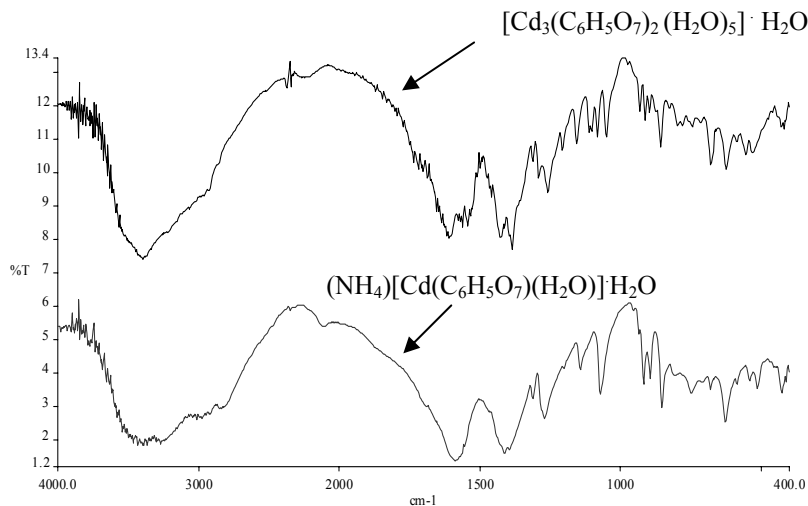


Fig. 2. FT-IR spectra of complexes $(\text{NH}_4)[\text{Cd}(\text{C}_6\text{H}_5\text{O}_7)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ and $[\text{Cd}_3(\text{C}_6\text{H}_5\text{O}_7)_2(\text{H}_2\text{O})_5] \cdot \text{H}_2\text{O}$

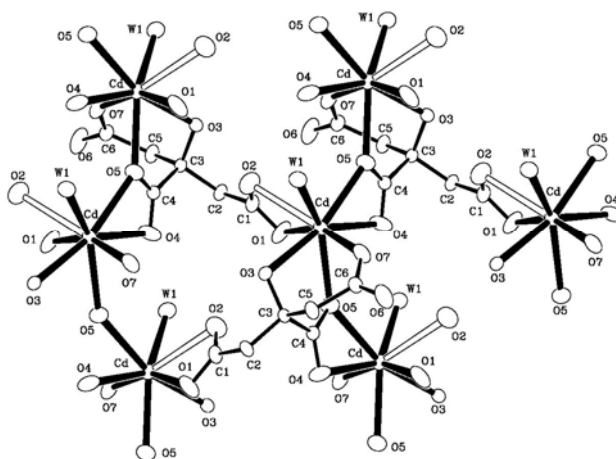


Fig. 3. ORTEP diagram of the mononuclear complex $(\text{NH}_4)[\text{Cd}(\text{C}_6\text{H}_5\text{O}_7)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$

Conclusions

In the course of the herein presented research, the ability of citric acid to promote complexation chemistry with Cd(II) was examined. Our studies were carried out in aqueous media and in a wide pH range. Cadmium reacted with citric acid in aqueous solution, at pH~3, and afforded formation the 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 $(\text{NH}_4)[\text{Cd}(\text{C}_6\text{H}_5\text{O}_7)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$. The two products were isolated in a crystalline form and were characterized structurally and spectroscopically. The observed reactivity pointed to structural features borne by Cd-citrate species in aqueous media. The potential relevance to biological effects of such low molecular mass species may ride on their physicochemical characteristics discovered in the course of this investigation.

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

Acknowledgments

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References

- Bevan, C.; Kinne-Saffran, E.; Foulkes, E. C.; Kinne, R. K. H. (1989). *Toxicol. Appl. Pharmacol.*, 101, 461-469.
- Glusker, J. P. (1980). *Acc. Chem. Res.*, 13, 345-352.
- Hue, N. V.; Craddock, G. R.; Adams, F. (1986). *Soil Sci. Soc. Am. J.*, 50, 28.
- Martin, R. B. (1986). *Inorg. Biochem.*, 28, 181-187.
- Matzapetakis, M.; Raptopoulou, C. P.; Tsohos, A.; Papaefthymiou, V.; Moon, N.; Salifoglou, A. (1998). *J. Am. Chem. Soc.*, 120, 13266-13267.