

AQUEOUS STUDIES OF THE BINARY Cr(III)-CITRATE SYSTEM

Catherine Gabriel¹, C. Mateescu², A. Salifoglou¹

¹Department of Chemical Engineering, Aristotle University of Thessaloniki,
Thessaloniki 54124, Greece, E-mail: salif@auth.gr

²Faculty of Food Processing Technology, Banat's University of Agricultural Sciences
and Veterinary Medicine, Timisoara, Romania. E-mail: c.mateescu@usab-tm.ro

Abstract

In the present study, two new aqueous Cr(III)-citrate species were synthesized. The new species were characterized by elemental analysis, spectroscopic, structural, thermal, EPR and magnetic susceptibility studies. Detailed aqueous speciation studies in the Cr(III)-citrate system suggest the presence of a number of species, among which is the mononuclear $[Cr(C_6H_5O_7)_2]^{3-}$ complex, optimally present around pH ~4.0-5.0.

Keywords: chromium(III), citric acid, speciation studies, structure, spectroscopic properties

Introduction

Chromium occurs in the environment mainly in the elemental state Cr⁰, and in compounds of Cr(III), the trivalent species, or hexavalent Cr(VI) (Sigel, 1995). In soils and sediments, chromium may be present in one of the two thermodynamically stable oxidation states: Cr(III) or Cr(VI) (James, 1983). Chromium(VI) constitutes a significant health hazard and the World Health organization has, therefore, established a limit of 0.05 mg/lit for Cr(VI) in drinking water (Sheehan, 1991). Compounds of Cr(VI) are generally more soluble in water than those of Cr(III). Chromium(III) presents a low health risk. The only significant toxicological threat from Cr(III) is its potential oxidation to Cr(VI) by Mn oxides (Johnson, 1991) or, at pH values greater than 9, by molecular oxygen (Krebs, 1937).

Chromium(III), as a metal ion, has a tendency to be absorbed specifically on clay and oxide surfaces and to hydrolyze within the

ordinary environmental pH range (pH 3-9). The majority of Cr(III) in soils and sediments, therefore, occurs as sparingly soluble hydroxy polymers adsorbed onto colloid surfaces.

There is considerable evidence indicating an essential role of Cr in the metabolism of higher animals (Bartelett, 1998). For instance, the impaired carbohydrate metabolism seen in Cr-deficient rats or humans can be corrected by administration of small amounts of the metal.

Low molecular mass organic acids (e.g. citrate, oxalate and tartrate) are among the best-characterized and abundant organic molecules in terrestrial and aquatic ecosystems (Liang, 1990).

One such organic acid is citric acid, which possesses structural characteristics that render it an excellent chelator in several binary and ternary systems with metal ions (Hue, 1986), resulting in the formation of soluble complexes. In turn, soluble complexes that turn bioavailable lead to (bio)chemical interactions at the cellular level that lay the foundations of Cr(III) toxicity.

Hence, the scope of the present study is the structural delineation of the interaction of Cr(III) with the physiological low molecular mass binder α -hydroxycarboxylic acids in aqueous media (Gabriel, 2007).

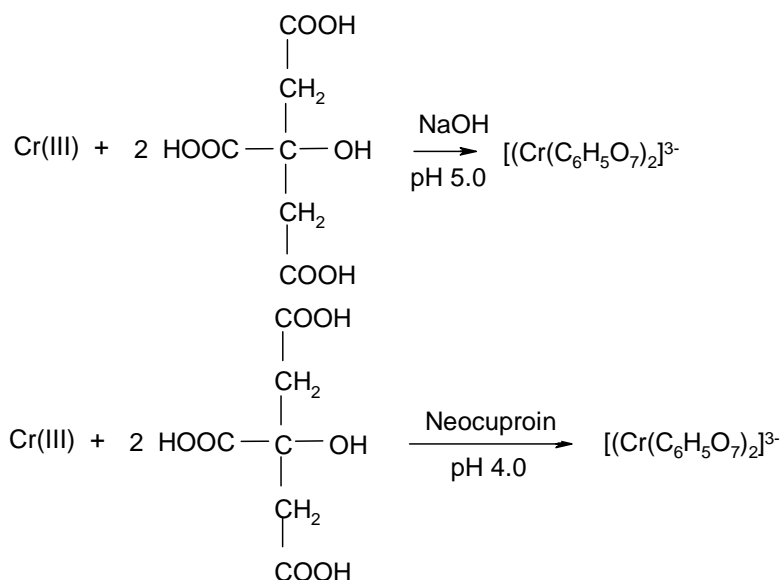
Experimental

In the course of this study, we investigated the aqueous synthetic chemistry of the binary chromium(III)-citric acid system.

The synthesis of $\text{Na}_3[\text{Cr}(\text{C}_6\text{H}_5\text{O}_7)_2] \cdot 9\text{H}_2\text{O}$ (**1**) was carried out in aqueous media, under specific pH conditions (sodium hydroxide was used to adjust the pH specifically at the value of 5). The addition of sodium hydroxide, for the adjustment of the pH, took place after one day of continuous stirring. Following addition of ethanol at 4°C, the reaction afforded pink crystals.

In a similar fashion, the synthesis of $[\text{Cr}(\text{C}_6\text{H}_5\text{O}_7)_2][\text{Hneo}]_6(\text{NO}_3)_2(\text{OH}) \cdot 15\text{H}_2\text{O}$ (**2**) was carried out in aqueous media, under specific pH conditions (neocuproin was used to adjust the pH at 4).

The stoichiometric reaction for the synthesis of complexes (**1**) and (**2**) of Cr(III) with citric acid are given below:



Results and Discussions

Positive identification on the crystalline products was achieved by elemental analysis, spectroscopic, structural, thermal, EPR and magnetic susceptibility studies.

The FT-IR spectra of the complexes were recorded in KBr and reflected the presence of vibrationally active carboxylate groups. Specifically, antisymmetric stretching vibrations $\nu_{\text{as}}(\text{COO}^-)$ were present for the carboxylate carbonyls in the range $1616\text{-}1579\text{ cm}^{-1}$ for **(1)** and in the range $1641\text{-}1603\text{ cm}^{-1}$ for **(2)**, respectively. Symmetric vibrations $\nu_{\text{s}}(\text{COO}^-)$ for the same groups were present around 1384 cm^{-1} for both **(1)** and **(2)**.

The UV/Visible spectrum of **1** and **2** were taken in water. The spectra shows a band around $\lambda_{\text{max}} 564\text{nm}$ ($\epsilon 27.8$). At higher energies, a band appears at $\lambda_{\text{max}} 351\text{ nm}$ ($\epsilon \sim 33.3$).

The structure of the complexes **(1)** and **(2)** is shown in Figure 1.

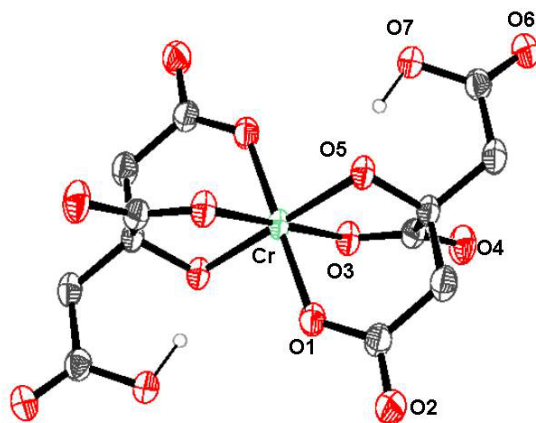


Figure 1. Structure of the anion in **1** and **2** with the atom-labeling scheme.

Conclusions

In the course of the herein presented research, the ability of citric acid to promote complexation chemistry with Cr(III) was examined in aqueous media. Following a pH-dependent approach in the synthesis of potential species arising in aqueous solution, Cr(III) reacted with citric acid, at pH~ 4.0-5.5, and afforded the mononuclear anions $[\text{Cr}(\text{C}_6\text{H}_5\text{O}_7)_2]^{3-}$, which were isolated with different counter ions in a crystalline form and were characterized structurally and spectroscopically. The physicochemical data on the new species formulate the physicochemical profile of Cr(III) in the specific binary system with citric acid and emphasize the structural and chemical features that could promote chemistries related to a beneficial or biotoxic role of that metal ion.

Acknowledgments

The present study is co-funded by European Union-European Social Fund and National fund PYTHAGORAS-EPEAEK II. The authors would also like to acknowledge the financial support to this project by a “PENED” grant from the General Secretariat of Research and Technology, Greece.

References

- Bartlett, R.J., (1998). *Characterizing soil redox behavior*. In: Sparks, D.L.(Ed.), *Soil Physical Chemistry*, second ed. CRC Press, Boca Raton, FL, pp. 371-397.
- Gabriel, C., Raptopoulou, C.P., Terzis, A., Tangoulis, V., Mateescu, C., Salifoglou, A. (2007). *Inorg. Chem.*, 46, 2998-3009.
- Hue, N.V., Craddock, G.R., Adams, F. (1986). *Soil Sci. Soc. Am. J.*, 50, 28.
- Krebs, H. A., Johnson, W. A. *Enzymologia*, **1937**, 4, 148-156.
- Liang, J., Madden, M., Shah, V.K., Burris, R.H. (1990). *Biochem.*, 29, 8577-8581.
- James, B.R., Bartlett, R.J. (1983). *J. Environ. Qual.*, 12, 173-176.
- Johnson, C.A., Xyla, A.G. (1991). *Geochim. Cosmochim. Acta.*, 55, 2861-2866
- Sheehan, P.J., Meyer, D.M., Sauer, M.M., Paustenbach, D.J. (1991). *J. Toxicol. Environ. Health*, 32, 161-201.
- Sigel, H., Sigel, A. (1995). *Metal Ions in Biological Systems*, Marcel Dekker, Inc., New York NY, pp. 186-187.

Aqueous Studies of the Binary Cr(III)-Citrate System