

A CHROMIUM(III)-CITRATE COMPLEX FROM AQUEOUS SOLUTIONS

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Abstract

Citric acid reacts with chromium(VI) in aqueous solutions. In the developing redox reaction, formation of Cr(III)-citrate complex takes place. In the present study, a new complex Cr(III)-citrate was synthesized. The new species was characterized by elemental analysis, FT-IR and X-Ray crystallography.

Keywords: *chromium(III), citric acid*

Introduction

Chromium occurs in the environment mainly in the elemental state Cr^0 or 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 are those of Cr(III). Chromium(III) presents only 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). Most of Cr(III) in soils and sediments, therefore, occurs as sparingly soluble hydroxy polymers sorbed onto colloid surfaces.

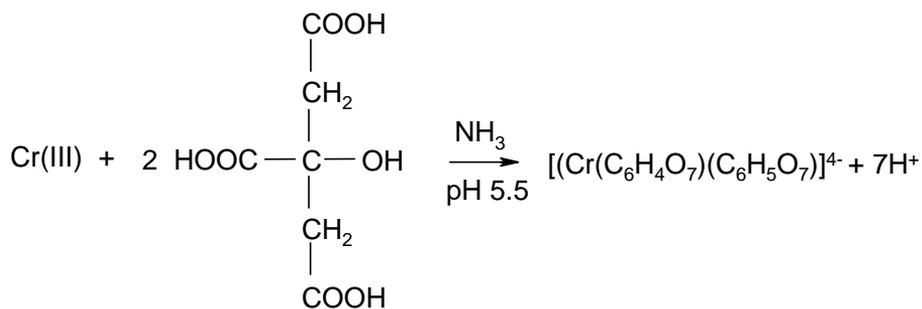
There is considerable evidence indicating an essential role of Cr in the metabolism of higher animals (Bartelett, 1998). For instance, the impaired carbohydrate metabolism seen in Cr-deficient rats or humans can be corrected by administration of small amounts of the metal. Cr(III) has also been identified and partially characterized as the glucose tolerance factor (GTF) believed to be essential for the normal disposition of glucose loads (Liang, 1990).

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. Citric acid 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. Hence, the scope of the present study on the interaction of Cr(III) with α -hydroxycarboxylic acids in aqueous media.

Experimental

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

The synthesis of $(\text{NH}_4)_4(\text{Cr}(\text{C}_6\text{H}_4\text{O}_7)(\text{C}_6\text{H}_5\text{O}_7)\cdot 3\text{H}_2\text{O}$ (**1**) was carried out in aqueous media, under specific pH conditions (ammonia was used to adjust the pH specifically at the value of 5.5-6.5) in the physiological pH range. The addition of ammonia, for the adjustment of the pH, took place after one day of continuous stirring. Following addition of ethanol at 4°C, the reaction afforded bluish crystals. The stoichiometric reaction for the synthesis of complex of Cr(III) with citric acid is given below:



Results and Discussion

Positive identification on the crystalline product was achieved by elemental analysis, FT-IR and X-Ray crystallography.

The FT-IR spectrum of the complex was recorded in KBr and reflected the presence of vibrationally active carboxylate groups. Specifically, antisymmetric stretching vibrations $\nu_{as}(\text{COO}^-)$ were present for the carboxylate carbonyls around 1583 cm^{-1} . Symmetric vibrations $\nu_s(\text{COO}^-)$ for the same groups were present in the range $1403\text{-}1372\text{ cm}^{-1}$.

The structure of the complex $(\text{NH}_4)_4(\text{Cr}(\text{C}_6\text{H}_4\text{O}_7)(\text{C}_6\text{H}_5\text{O}_7)\cdot 3\text{H}_2\text{O})$ is presented in Figure 1. The H atom shown is hydrogen bonded to O17, so chains along the α -axis are formed. The lattice structure is much more complicated due to H-bonding interactions between the ammonium counterions and water molecules in the lattice.

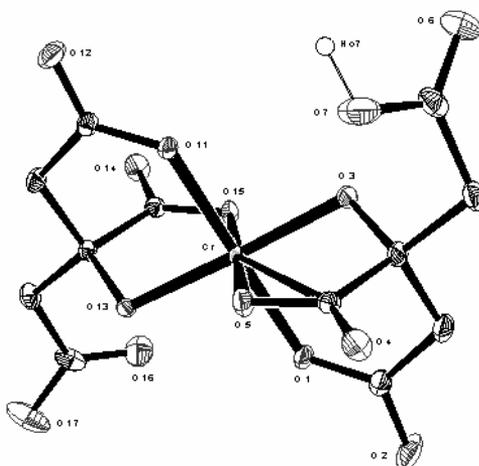


Fig. 1. Structure of **1** with the atom-labeling scheme. Thermal ellipsoids are drawn by ORTEP and represent 40% probability surfaces.

Conclusions

In the course of the herein presented research, the ability of citric acid to promote complexation chemistry with Cr(III) was examined. Our synthetic studies were carried out in aqueous media and in a wide pH range. Chromium(III) reacted with citric acid in aqueous solution, at pH~5.5, and afforded the mononuclear anion $[\text{Cr}(\text{C}_6\text{H}_4\text{O}_7)(\text{C}_6\text{H}_5\text{O}_7)]^{4-}$, which was isolated in a crystalline form and was characterized structurally and spectroscopically.

Acknowledgments

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