

SYNTHESIS, STRUCTURAL AND SPECTROSCOPIC CHARACTERIZATION OF A NEW Cr(III)-CITRATE COMPLEX. RELEVANCE TO CHROMIUM TOXICITY

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Abstract

In the present study, a new aqueous Cr(III)-citrate complex was synthesized. The new species was 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 $[\text{Cr}(\text{C}_6\text{H}_4\text{O}_7)(\text{C}_6\text{H}_5\text{O}_7)]^{4-}$ complex, optimally present around pH ~5.5.

Keywords: chromium(III), citric acid, speciation studies

Introduction

Chromium occurs in the environment mainly in the elemental state Cr^0 , 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). The majority of Cr(III) in soils and sediments, therefore, occurs as sparingly soluble hydroxy polymers adsorbed onto colloid surfaces.

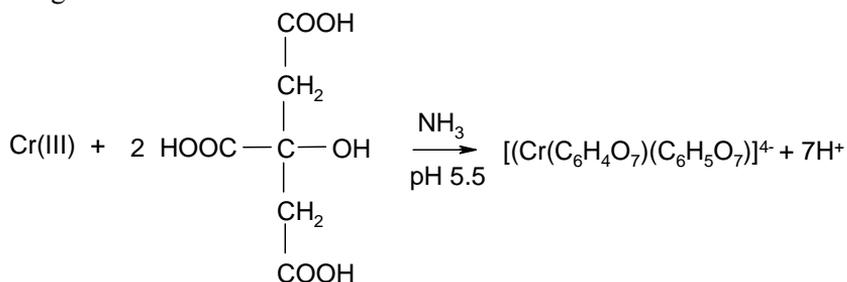
There is considerable evidence indicating an essential role of Cr in the metabolism of higher animals (Bartlett, 1998). For instance, the impaired carbohydrate metabolism seen in Cr-deficient rats or humans can be corrected by administration of small amounts of the metal. Cr(III) has also been identified and partially characterized as the glucose tolerance factor (GTF) believed to be essential for the normal disposition of glucose loads (Sigel, 1995).

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 ruin 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.

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). 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, spectroscopic, structural, thermal, EPR and magnetic susceptibility studies. 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 UV/Visible spectrum of **1** was taken in water. The spectrum shows a band around $\lambda_{\text{max}} = 570\text{ nm}$ ($\epsilon\ 27.8$). At higher energies, a shoulder-like band appears at 450 nm ($\epsilon\ \sim 22$), ultimately reaching a well-formed major peak at $\lambda_{\text{max}} = 393\text{ nm}$ ($\epsilon\ 33.3$). A very weak shoulder-like band appears at 318 nm ($\epsilon\ \sim 9$) subsequently rising into the UV region. In the ultraviolet region, a clear band shows up at 270 nm ($\epsilon\ 244.5$).

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 a -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.

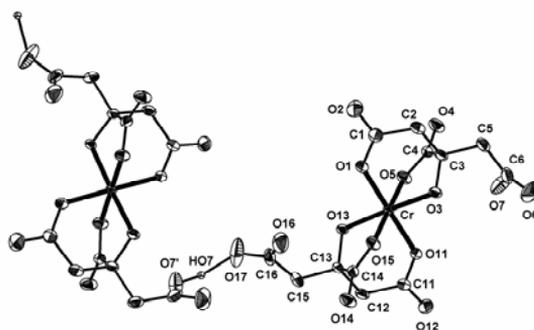


Fig. 1. Structure of **1** with the atom-labeling scheme. Thermal ellipsoids are drawn by ORTEP and represent 40% probability surfaces.

Potentiometric titrations of the ligand citric acid alone, and Cr(III) with citric acid in various metal ion to ligand molar ratios were carried

out. The titration curves were evaluated with different potential speciation models. Complex **1** occurs at the titration curves at pH 5.5 with the form $[\text{CrL}_2\text{H}_1]^{4+}$, ($\text{L} = \text{C}_6\text{H}_5\text{O}_7^{3-}$), which is in good agreement with $\text{Cr}[\text{Cr}(\text{C}_6\text{H}_4\text{O}_7)(\text{C}_6\text{H}_5\text{O}_7)]^{4+}$.

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~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. 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

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