AN IN-DEPTH INVESTIGATION OF THE STRUCTURAL SPECIATION IN THE BINARY Ti(IV)-CITRIC ACID AQUEOUS SYSTEM. RELEVANCE TO FOOD AND HEALTH

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Abstract

Titanium is a transition metal, which has found widespread applications in medicine, food industry and agriculture. Its increasing contact with biological tissues in humans has brought considerable attention to the consequences of the requisite (bio)chemistry in human health. Being aware of the interactions developing between that metal and various biological components throughout the living kingdom, the structural speciation of Ti(IV)-citric acid system has been studied and key pH-variants have been synthesized and characterized physicochemically.

Key words: titanium, citric acid, structural speciation

Introduction

Titanium is a well-known transition metal widely encountered in various industries. To that end, titanium, in the form of various metal alloys, has since long been employed in surgical rectification devices to remedy malformation or bone-problems in humans.

Titanium is one of the most rugged metals. However, the lowering of its price and an increased availability has made this material suitable for use in other fields, such as the food industry. In that sense, several studies have been reported and numerous assessments have been made on titanium being regarded as a candidate food-grade material.

Concurrently, titanium (Ti) has been reported to exhibit significant biological effects on plants, being beneficial at low and toxic at higher concentrations. To this end, results of hydroponic experiments with oats have proposed that the effect called hormesis is the mechanism of
Ti action in plants. In another application, Ti(IV)-ascorbate was sprayed on plum trees in several combinations with other commercial compounds containing Ca(II) and Mg(II). The beneficial effects observed were attributed on Ti absorption, translocation and assimilation processes.

In all of the aforementioned cases, it appears that titanium comes in contact with biological components, like citric acid, at the cellular level. Hence, the need arises to investigate the interactions of Ti(IV) with physiological components, thus enabling delineation of the requisite effects and their repercussions to the general health of the organisms and humans involved. To this end, the binary system Ti(IV)-citric acid was studied synthetically and key species were isolated and examined spectroscopically.

**Experimental**

The synthesis of the new complexes Na$_6$[Ti(C$_6$H$_5$O$_7$)$_2$(C$_6$H$_4$O$_7$)] · 16H$_2$O (1) and Na$_3$(NH$_4$)$_3$[Ti(C$_6$H$_5$O$_7$)$_2$(C$_6$H$_4$O$_7$)] · 8.5H$_2$O (2) was achieved in water under pH specific conditions. Addition of aqueous sodium hydroxide in 1 and equal amounts of aqueous ammonia and sodium hydroxide in 2, raised the pH of the solution to ~6.0, and concurrently provided the necessary counterions for the subsequently derived anionic complex. The resulting colorless solution was treated with ethanol at 4°C and afforded efficiently colorless crystalline materials.
Results and Discussions

Analytical, spectroscopic and finally X-ray crystallographic techniques (Figure 1) revealed the identity of the new species at a near physiological pH value. FT-IR spectroscopy was essential in pointing out the coordination of citric acid to the metal ion Ti(IV). $^{13}$C-NMR spectroscopy in the solid state was equally informative on the coordination mode of citrate to Ti(IV). In combination with solution $^{13}$C- and $^1$H-NMR spectroscopy significant details were discovered about the solution behavior of the title species in comparison with their structure in the solid state. As a discrete species, complexes 1 and 2 arose out of aqueous media to project a very distinct picture of a) the mode of citrate coordination b) the degree of protonation of the three citrate ligands around the central metal ion, and c) the concomitantly formulated octahedral geometry around Ti(IV). Most important of all, however, was the variable protonation state of the bound citrate ligands around Ti(IV). Specifically, two of the bound citrates were triply deprotonated, while the third one was fully deprotonated.

![Fig. 1. ORTEP diagram of the [Ti(C_6H_5O_7)_2(C_6H_4O_7)]^{6-} anion with the atom labelling scheme in 1.](image-url)
Conclusions

Collectively, the synthetic efforts targeting Ti(IV)-citrate complexes from aqueous solutions have contributed significantly in delineating the nature of a number of such species arising in the course of pH-dependent reactions. Each such well-characterized species reflects the power of the synthetic chemistry in delivering structurally and spectroscopically characterized Ti(IV)-citrate complexes, thus enabling elucidation of the requisite aqueous distributions prior to any relevant speciation studies. To this end, the contribution of the synthetic chemistry to the structural speciation of the binary system Ti(IV)-citrate is undisputed. Moreover, it offers detailed physicochemical information, which would help establish the basis of understanding of potential interactions of Ti(IV) with biologically relevant molecules.

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References