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SYNTHESIS AND CHARACTERIZATION OF TWO NEW ISOSTRUCTURAL IRON(III)-QUINATES FROM AQUEOUS SOLUTIONS

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Abstract

Two new iron(III)-quinate complexes were synthesized in aqueous solutions at the optimum pH 3. They were isolated in pure crystalline form and characterized by elemental analysis, spectroscopic techniques (EPR, FT-IR), magnetic studies and X-ray crystallography. The new species contains iron ions in an octahedral environment, where each iron ion coordinates to three quinic acids. The collective physicochemical properties of the derived species project fundamental chemical and structural properties of Fe(III)-hydroxycarboxylate interactions akin to biochemical processes of importance to cellular physiology or aberrant activity.

***Keywords**: Iiron(III), D-(-)-quinic acid*

Introduction

Iron is the most abundant metal on Earth, and is believed to be the tenth most abundant element in the universe. It is encountered in a wide range of systems in all living organisms (bacteria as well as plants or mammals) in both Fe(II) and Fe(III) forms (Gautier-Luneau, 2005) and it plays various roles in many important life processes (Lippard, 1994). More specifically, mineral nutrition is extremely important in plants for growth and development, and iron is one of these minerals. Moreover, iron is also indirectly responsible for much of the green color of growing plants, because of its role in the production of chlorophyll (Sigel, 2005).

D-(-)-Quinic acid, (-)-1α,3α,4α,5β-tetra-hydroxy-1-cyclohexane-carboxylic acid, is an organic carboxylic acid binder widely found in plants (Bohm, 1965; Corse, 1966; Kelley, 1976) acid is a polyfunctional molecule, which can coordinate to metalloelements in a variety of ways.

In an effort to delineate the role of Fe(III) in interactions with biologically significant targets, we have explored the relevant synthetic aqueous chemistry. Through that, we hoped to develop a good understanding of the requisite chemistry and its linkage to iron uptake by human body as well as by plants.

Experimental

We investigated the aqueous chemistry of binary system $FeCl_3 \cdot 6H_2O$-D-(-)-quinic acid, where under specific stoichiometric conditions, reactions led to the isolation of two new isostructural species:

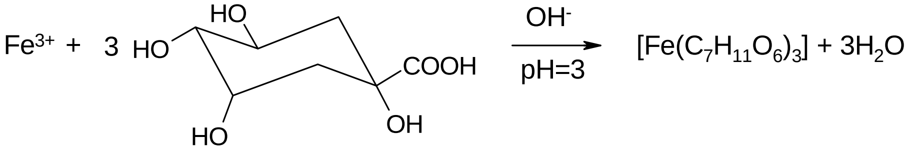
$(NH_4)[Fe(C_7H_{11}O_6)_3] \cdot (OH) \cdot 1.5H_2O$ (**1**)

$K[Fe(C_7H_{11}O_6)_3] \cdot (OH) \cdot 3H_2O$ (**2**).

Both reactions were investigated at the pH 3, 5 and 9, but the optimum pH was 3. Addition of ammonia and KOH for the adjustment of the pH, resulted in the isolation of the two isostructural species. The resulting reaction mixture in each case was placed in the refrigerator at 4°C. Following several days of standing under those conditions, each reaction afforded yellow crystals, which were collected by filtration. The crystalline solids have proven to be stable in the air for long periods of time.

Results and Discussions

The stoichiometric reaction for the synthesis of the two species of Fe(III) with D(-)-quinic acid is given below:



quinic acid

Elemental analysis pointed to the molecular formulation $(NH_4)[Fe(C_7H_{11}O_6)_3] \cdot (OH) \cdot 1.5H_2O$ (MW = 691.40): C, 36.4; H, 5.93;

N, 2.1; Found: C, 34.28; H, 6; N, 2.3. Elemental analysis pointed to the molecular formulation $K[Fe(C_7H_{11}O_6)_3]\cdot(OH)\cdot 3H_2O$ (MW = 739.48): C, 34.7; H, 5.4; Found: C, 34.93; H, 5.6.

Complex (**1**) and (**2**) were further characterized by FT-IR and X-Ray crystallography on one of the isolated crystals from each case.

The FT-IR spectrum of the inorganic-organic hybrid was recorded in KBr and reflected the presence of vibrationally active carboxylate groups. The antisymmetric stretching vibrations for complex (**1)** $\nu_{as}(COO^-)$ appear in the range from 1666 up to 1635cm^{-1}, whereas the symmetric stretches $\nu_s(COO^-)$ appear in the range 1400-1332 cm^{-1}. The antisymmetric stretching vibrations for complex (**2)** $\nu_{as}(COO^-)$ appear in the range from 1660 up to 1637cm^{-1}, whereas the symmetric stretches $\nu_s(COO^-)$ appear in the range 1385-1330 cm^{-1}.

The UV/Visible spectrum of **2** was taken in water. The spectrum shows a band around λ_{max} = 354 nm (ε 1572). At higher energies, a shoulder-like band appears at 334 nm (ε 1587). A very well-formed major peak appears around 229 nm (ε 2652), subsequently rising into the visible region. Due to the greater oxidizing power of Fe(III), ligand to metal charge transfer bands are the predominant features in the electronic spectrum.

The structure of the isostructural complexes **1** and **2** are presented in Figure 1. Each Fe(III) atom coordinates to three quinic acids in an octahedral environment. The addition of ammonia and KOH, as bases, was crucial for the arisen of the pH.

Potentiometric titrations of the metal ion and of the ligand alone were carried out. Moreover, Fe(III) with quinic acid in various metal ion to ligand molar ratios were also carried out. The titration curves were evaluated with different potential speciation models.

Conclusions

The syntheses, isolation, spectroscopic and structural characterization of **1** and **2** provide a clear case of an interaction of quinate with iron(III), leading to new materials. The collective physicochemical properties of these materials a) exemplify the importance of structural and chemical attributes of Fe(III)-(O) ligand species arising as a result of the requisite interactions in aqueous media, and b) project types of interactions of Fe(III) with related low as well as high molecular mass targets in cellular fluids, leading to cellular physiological effects of aberrant biological processes. These and other likely elusive interactions between Fe(III) and low molecular mass α-hydroxycarboxylate ligand interactions in biologically relevant media are currently being investigated at the molecular chemical level.

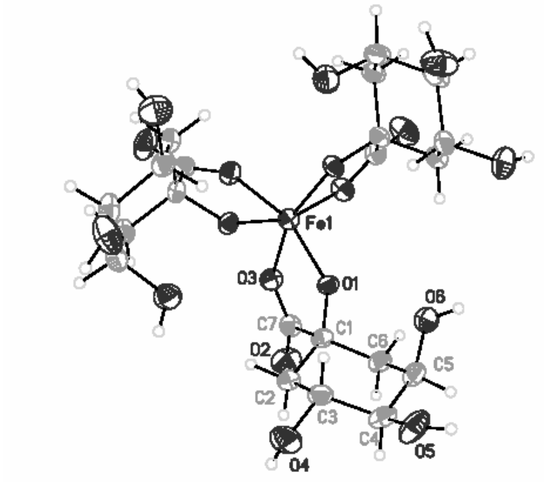


Fig. 1. ORTEP diagram of the complex $[Fe(C_7H_{11}O_6)_3]^0$.

Acknowledgments

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