

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

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Abstract

In the present study, a new complex Cr(III)-quinic 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)-quinic system suggest the presence of a number of species with distinct structural properties related to the ones encountered in the synthetic complex isolated and investigated.

Keywords: *chromium(III), quinic acid, speciation studies*

Introduction

Chromium is one of the abundant elements in the earth's crust. It is present in abiotic as well as biological systems (Bae, 2005). As a metal it is used in various industrial processes, like tanneries, cement industries, plating and alloying industries, and corrosive paints (Ramos, 1994). It is also used to improve the non-linear optical properties of key oxide materials (Földvári, 1991) as a dopant (Peter, 1996), modifying the efficiency and lifetime of the photorefractive signals (i.e. the "memory" -type signals in connection with hologram recording) (Földvári, 1995). Equally significant is the presence of chromium in binary metal oxides, which are catalytically active materials, finding a wide variety of uses including supports for heterogeneous catalysts, electrochromic devices and, more recently, gas sensors (Moseley, 1991; Schierbaum, 1991; Meixner, 1996).

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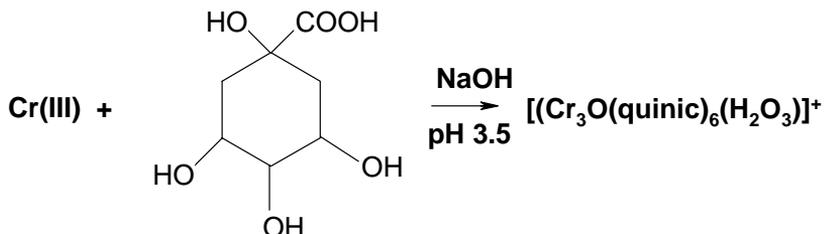
There is considerable evidence indicating an essential role of Cr in the metabolism of higher animals (Bartlett, 1998). For instance, the impaired carbohydrate metabolism seen in Cr-deficient rats or humans can be corrected by administration of small amounts of the metal. Cr(III) has also been identified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

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

In an effort to delineate the role of Cr(III) in interactions with biologically significant targets, we have explored the relevant synthetic aqueous chemistry with the physiological substrate quinic acid. To this end, we herein report on the pH-specific synthesis, spectroscopic and structural characterization, and magnetic susceptibility studies of a new aqueous binary Cr(III)-quinic species arising from the requisite binary system.

Experimental

In the course of this study, we investigated the aqueous synthetic chemistry of the binary chromium(III)-quinic acid system. The synthesis of $\text{Na}[\text{Cr}_3\text{O}(\text{quinic})_6(\text{H}_2\text{O})_3](\text{NO}_3)_{1.5}(\text{OH})_{0.5} \cdot 6.5\text{H}_2\text{O}$ (**1**) was carried out in aqueous media, under specific pH conditions (Sodium hydroxide was used to adjust the pH in the range 3.5-5.5). 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 bluish crystals. The stoichiometric reaction for the synthesis of complex **1** between Cr(III) and quinic acid is given below:



Results and Discussions

Positive identification on the crystalline product was achieved by elemental analysis, spectroscopic, structural, thermal, EPR, magnetic susceptibility studies and aqueous speciation 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 $\nu_{\text{as}}(\text{COO}^-)$ were present for the carboxylate carbonyls around 1627 cm^{-1} . Symmetric vibrations $\nu_{\text{s}}(\text{COO}^-)$ for the same groups were present in the range $1434\text{-}1383 \text{ cm}^{-1}$.

The UV/Visible spectrum of **1** was taken in water. The spectrum shows a band around $\lambda_{\text{max}} = 586 \text{ nm}$ (ϵ 52). At higher energies, a well-formed major peak appears at 438 nm (ϵ 63). The structure of the complex $\text{Na}[\text{Cr}_3\text{O}(\text{quinic})_6(\text{H}_2\text{O})_3](\text{NO}_3)_{1.5}(\text{OH})_{0.5} \cdot 6.5\text{H}_2\text{O}$ (**1**) is presented in Figure 1. The Cr(III) atoms are coordinated with the quinic ligand only by the carboxylate group and between them with an oxygen atom. The lattice structure is much more complicated due to H-bonding interactions between the water molecules in the lattice.

Potentiometric titrations of the ligand quinic acid alone, and Cr(III) with quinic acid in various metal ion to ligand molar ratios were carried out. The titration curves were evaluated with different potential speciation models. The best fit between the experimental and calculated titration curves for the binary Cr(III)–quinic acid system was obtained by considering the species $[\text{CrLH}_2]^{3+}$ ($\text{LH}_2 = \text{C}_7\text{H}_{12}\text{O}_7$), $[\text{CrLH}]^{4+}$ ($\text{LH} = \text{C}_7\text{H}_{11}\text{O}_7^-$), $[\text{CrLH}_2]^{1-}$, $[\text{CrL}_2\text{H}_2]^{1+}$, $[\text{CrL}_2\text{H}_1]^0$. At a first glimpse, it appears that the trinuclear species **1**, synthesized and

isolated through this work, is not represented in the collection of species identified in the distribution scheme derived.

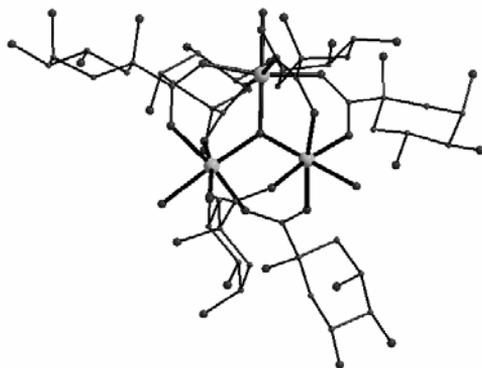


Fig. 1. Structure of $\text{Na}[\text{Cr}_3\text{O}(\text{quinic})_6(\text{H}_2\text{O})_3](\text{NO}_3)_{1.5}(\text{OH})_{0.5}\cdot 6.5\text{H}_2\text{O}$ (**1**).

This seemingly different behavior between the solid state nature in species **1** and the solution speciation of the binary system Cr(III)-quinic acid may reflect a more complex behavior of the system exemplified through the aqueous interactions of Cr(III) with quinic acid. Such interactions and associated species are in further need of perusal and are currently under investigation in our labs.

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 quinic acid in aqueous solution, at pH~3.5, and afforded the trinuclear cation $[\text{Cr}_3\text{O}(\text{quinic})_6(\text{H}_2\text{O})_3]^+$, which was isolated in a crystalline form and was characterized structurally and spectroscopically. Comparison between the synthetic trinuclear complex **1** and the collection of species in the aqueous distribution of the binary Cr(III)-quinic acid system reveals the complexity of interactions of the two components and necessitates further perusal of species and associated physicochemical properties linked to that metal ion's biological behaviour.

Acknowledgments

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References

- Bae, W.-C., Lee, H.-K., Choe, Y.-C., Jahng, D.-J., Lee, S.-H., Kim, S.-J., Lee, J.-H., Jeong, B.-C. (2005). *J. Microbiology* 43, 21-27.
- 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.
- Bohm, B. A. (1965). *Chem. Rev.* 65, 435.
- Corse, J., Lundin, R.E., Sondheimer, E., Waiss, A.C. (1966). *J. Photochem.* 5, 767.
- Földvári, I., Scripsick, M.P., Halliburton, L.E., Pèter, À. (1991). *Phys. Lett. A* 154, 84.
- Földvári, I., Pèter, À., Powell, R.C., Taheri, B. (1995). *Opt. Mater.* 4, 299.
- Kelley, C.J., Harruff, R.C., Carmack, M. (1976). *J. Org. Chem.* 41, 449.
- Meixner, H., Lampe U. (1996). *Sens. and Actuators B.* 33, 198–202.
- Moseley, T., Norris, J.O.W., Williams, E. (1991). *Techniques and Mechanisms in Gas Sensing*, I.O.P. Publishing, Bristol; Adam Hilger Series on Sensors
- Pèter, À., Szakács, O., Földvári, I., Bencs, L., Munoz, A.F. (1996). *Mater. Res. Bull.* 31, 1067.
- Ramos, R.L., Martinez, A.J., Coronado, R.M.G. (1994). *Water Sci. Technol.* 30, 191.
- Schierbaum, K.D., Weimar, U., Gopel, W. (1991). *Sens. and Actuators B.* 3, 205–214.

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