M. Menelaou, et all. Journal of Agroalimentary Processes and Technologies,
Volume XII, No. 2 (2006), 561-564
Communication - Food Science Section

SYNTHESIS AND CHARACTERIZATION OF A NEW Ni(II)-QUINATE COMPLEX FROM AQUEOUS SOLUTIONS. FROM THE AQUEOUS SPECIATION TO Ni(II) TOXICITY

Melita Menelaou,[1] C. Mateescu,[2] A. Salifoglou[1,3]
[1]Department of Chemical Engineering, Aristotle University of Thessaloniki, Thessaloniki 54124, Greece
[2]Faculty of Food Processing Technology, Banat's University of Agricultural Sciences and Veterinary Medicine, Timisoara, Romania.
[3]Chemical Process Engineering Research Institute, Thermi, Thessaloniki 57001, Greece

Abstract

A new Ni(II)-quinate species was synthesized in aqueous solution at the optimum pH = 5. It was isolated in a pure crystalline form and was characterized by elemental analysis, spectroscopic techniques (FT-IR, UV-Vis), magnetic studies and X-ray crystallography. The new species contains nickel ions in an octahedral environment, where each nickel ion coordinates with three quinic acids. The aqueous speciation work, accompanying the synthetic efforts, project a complex picture of the related aqueous synthetic work and relate to Ni(II)-(O,N)-containing biological interactions of importance to cellular integrity and physiology.

***Keywords**: Nickel(II), D-(-)-Quinic acid*

Introduction

Nickel, as an abundant natural element, is recognized as an essential trace element for bacteria, plants, animals and humans (Halcrow, 1994). It can be combined with other metals, such as iron, copper, chromium to form alloys. Moreover, it is encountered in a wide range of biological systems as well as in all types of soil. In the biological systems, many hydrogenases contain nickel in addition to iron-sulfur clusters (Bouwman, 2005). The nickel enzymes CODH and ACS, for example, play an important role in carbon cycling (Evans, 2005).

D-(-)-Quinic acid, (-)-1α,3α,4α,5β-tetra-hydroxy-1-cyclohexane-carboxylic acid, is 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. It is known that cyclic polyols act as calcium carriers in biological systems.

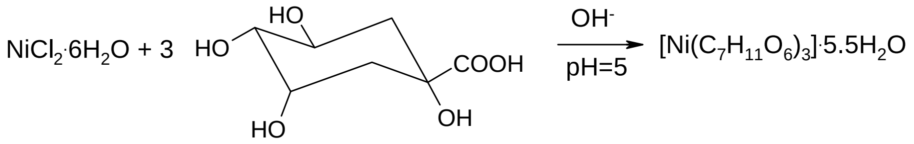
Experimental

We investigated the aqueous synthetic chemistry of the binary system $NiCl_2.4H_2O$-D-(-)-Quinic acid. There, under specific stoichiometric conditions and numerous reactions, the arisen reactivity led to the isolation of the new species $Na[Ni(C_7H_{11}O_6)_3]\cdot 5.5H_2O$ (**1**).

More specifically, the synthesis of $Na[Ni(C_7H_{11}O_6)_3]\cdot 5.5H_2O$ was carried out in aqueous media (nanopure water was used for all reactions). The pH was adjusted to 5.5 with NaOH. The resulting reaction mixture was placed in the refrigerator at 4°C. Following several months of standing under those conditions, green crystalline material appeared on the bottom of the flask.

Results and Discussions

The stoichiometric reaction for the synthesis of the new complex of Ni(II) with D(-)-quinic acid is given below:



quinic acid

Elemental analysis pointed to the molecular formulation $Na[Ni(C_7H_{11}O_6)_3]\cdot 5.5H_2O$ (MW = 704.47). Yield: 30%. Anal. Calcd for **1**: C, 35.7; H, 5.43. Found: C, 34.91; H, 5.79. Complex **1** was further characterized by FT-IR and X-Ray crystallography for one of the isolated single crystal from the reaction mixture.

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 $\nu_{as}(COO^-)$ appear in the range $1600cm^{-1}$, whereas the symmetric stretches $\nu_s(COO^-)$ appear in the range $1442\text{-}1322\ cm^{-1}$.

The UV/Visible spectrum of **1** was taken in water. The spectrum shows a band around $\lambda_{max} = 725$ nm (ε 2). At higher energies, another band appears at around 662 nm (ε 2). Finally, a well-formed major peak appears at $\lambda_{max} = 395$ nm (ε 6).

X-Ray crystallography was instrumental in revealing the three dimensional structure of the investigated molecules. The structure of complex $Na[Ni(C_7H_{11}O_6)_3] \cdot 5.5H_2O$ is presented in Figure 1. Each Ni(II) ion coordinates to three quinic acids in an octahedral environment. The addition of NaOH, as a base, was crucial in the investigated reaction. Not only does that help adjust the pH of the reaction mixture, but also provides the ligands for Ni(II) with the appropriate counter ions needed to balance the arisen charge.

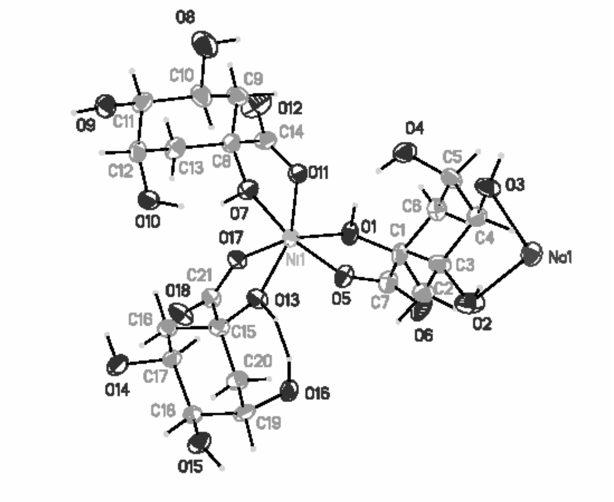


Fig. 1. ORTEB diagram of the $Na[Ni(C_7H_{11}O_6)_3] \cdot 5.5H_2O$

Potentiometric titrations of the metal, Ni(II) and the ligand alone were carried out. In addition to this, potentiometric titrations were also performed in different metal ion to ligand molar ratios. The titration curves were evaluated with different potential speciation models. Initial examination of the arisen aqueous speciation reveals that complex **1** doesn't appear to be one of the speciation components in the optimal model chosen. That observation projects the complex picture of the aqueous speciation of the binary Ni(II)-quinic acid. In turn that requires more in-depth perusal of the requisite aqueous speciation that will undoubtedly lead to a better understanding of the interactions of Ni(II) with low molecular α-hydroxycarboxylate substrates, such a quinic acid.

Conclusions

In this presented research, the ability of quinic acid to promote the aqueous complexation chemistry with Ni(II) was examined. The synthesis of **1**, its isolation, spectroscopic and structural characterization provides a clear picture of the structural and chemical features of the interaction of quinate with nickel. In so doing, the emerging information leads to a well-defined species distribution of Ni(II), which can interact with O-containing substrates of variable size and molecular mass. It is in this respect that the arisen species constitute the basis of the exploration of the structural speciation of the investigated binary system that bears relevance to Ni(II) aqueous toxicity.

Acknowledgments

The authors would like to acknowledge the financial support to this project by a “Pythagoras” grant from the National Ministry of Education and Religious Affairs and by a “PENED” grant from the General Secretariat of Research and Technology, Greece.

References

Bohm, B.A. (1965). *Chem. Rev. 65*, 435-440

Bouwman, E. Reedijk, J. (2005). *Coord. Chem. Rev. 249*, 1555-1581

Corse, J., Lundin, R. E., Sondheimer, E., Waiss, A.C. (1966). *J. Photochem. 5*, 767-772

Evans, D.J. (2005). *Chem. Rev. 249*, 1582-1595

Halcrow, M.A., Christou, G. (1994). *Chem. Rev. 94*, 2421-2481

Kelley, C.J., Harruff, R.C., Carmack, M. (1976). *J. Org. Chem. 41*, 449-452