THE SYNTHESIS, ISOLATION AND SPECTROSCOPIC CHARACTERIZATION OF A NEW Ni(II)-HYDROXYCARBOXYLATE COMPLEX. STEPS TOWARD UNDERSTANDING OF Ni(II) TOXICITY

Melita Menelaou, C. Mateescu, A. Salifoglou

1 Department of Chemical Engineering, Aristotle University of Thessaloniki, Thessaloniki 54124, Greece
2 Faculty of Food Processing Technology, Banat University of Agricultural Sciences and Veterinary Medicine, Timisoara, Romania.

Abstract

A new Ni(II)-hydroxy-carboxylate complex was synthesized in aqueous solution. D-(-)quinic acid, a α-hydroxycarboxylate ligand, interacted with Ni(II) at pH 5.5. The crystalline product was isolated and was characterized by elemental analysis, spectroscopic techniques (FT-IR, UV-Vis), magnetic studies and X-ray crystallography. The aqueous speciation work projects a complex picture of the related aqueous synthetic work and relates Ni(II) to biological interactions involved in cellular physiology.

Keywords: Nickel(II), Hydroxycarboxylate ligands, D-(-)-Quinic acid, toxicity

Introduction

Nickel is an abundant natural element, which is recognized as an essential trace element for bacteria, plants, animals and humans (Halcrow, 1994). It can also be used to manufacture alloys, stainless steel and coins with other metals, such as iron and copper. Moreover, Ni(II) is encountered in a wide range of biological systems as well as in all types of soil. In biological systems, nickel exists as an inorganic cofactor, in addition to iron-sulfur clusters (Bbouwman, 2005). In this regard, 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, as an α-hydroxycarboxylate physiological ligand is widely found in plants (Bohm, 1965; Kelley, 1976; Corse, 1966). In addition, quinic acid as a polyfunctional molecule, it can coordinate to metalloelements in a variety of ways. It is known that cyclic polyol act as calcium carriers in biological systems. Quinic acid contains all
of the aforementioned attributes and constitutes a natural target for essential metal ions such as Ni(II). To this end, investigating the aqueous interactions of Ni(II) with quinic acid was the crux of the efforts aiming at comprehending the intricate role the metal ion plays in natural biological systems.

**Experimental**

The aqueous synthetic chemistry of the binary system NiCl₂.4H₂O-D(-)-Quinic acid was investigated. Under specific pH-conditions, the arisen reactivity led to the isolation of the new species Na[Ni(C₇H₁₁O₆)₃]·2.75H₂O (I).

The pH-dependent synthesis of Na[Ni(C₇H₁₁O₆)₃]·2.75H₂O was carried out in aqueous media. The pH was adjusted to 5.5 with NaOH. The Ni(II)-quinate compound was isolated in pure crystalline form upon addition of ethanol to the reaction mixture at 4°C. The stoichiometric reaction for the synthesis of the new complex of Ni(II) with D(-)-quinic acid is given below:

\[
\text{Ni}^{II} + 3 \text{Na}^{+} \cdot \text{Ni}^{III} \cdot 3 \text{H}₂\text{O} \overset{\text{pH 5.5}}{\longrightarrow} 3 \text{OH}^- \]

D(-)-quinic acid  \[\rightarrow\]  [Ni(C₇H₁₁O₆)₃]⁻ + 3 H₂O  \[\text{Reaction 1}\]

Elemental analysis of the isolated green-colored crystalline material suggested the molecular formula Na[Ni(C₇H₁₁O₆)₃]·2.75H₂O for I. (MW=704.47). Yield: 30%. Anal. Calcd for I: C, 35.7; H, 5.5. Found: C, 35.0; H, 5.8. Complex I was further characterized by FT-IR and X-Ray crystallography on the isolated single crystals from the reaction mixture.

The FT-IR spectrum of I exhibits strong absorptions for the carbonyls of the carboxylate groups in both the antisymmetric and symmetric vibration regions. The antisymmetric stretching vibrations νₘ(COO⁻) appear close to 1602 cm⁻¹, whereas the symmetric stretches νₛ(COO⁻) appear in the range 1450-1334 cm⁻¹. The frequencies for the carbonyl stretches in I are shifted to lower values compared to those of
the free quinic acid, thus denoting the presence of the bound ligand to the metal ion.

The UV/Visible spectrum of 1 was recorded in water. The spectrum exhibits peaks at $\lambda_{\text{max}}$ 725 ($\varepsilon$ 2 M$^{-1}$cm$^{-1}$) and 662 nm ($\varepsilon$ 2 M$^{-1}$cm$^{-1}$), and a distant shoulder around 395 nm rising into the UV.

X-Ray crystallography was instrumental in revealing the three dimensional structure of the investigated molecules. The structure of complex Na[Ni(C$_7$H$_{11}$O$_6$)$_3$]2.75H$_2$O is presented in Figure 1. In the presence of Ni(II), the $\alpha$-alcoholic group retains its proton upon binding of the quinate group to the metal ion. Each binding site around Ni(II) includes the oxygen from the carboxylate moiety bearing 1-charge, thus raising the total charge for the mononuclear complex to 1-.

Formation of a five-membered metallacyclic ring is most likely a source for stability in the arising complex. The negative charge on the anionic complex [Ni(C$_7$H$_{11}$O$_6$)$_3$]$^-$ is counteracted by one sodium ion.

Figure 1. ORTEB diagram of the anion in Na[Ni(C$_7$H$_{11}$O$_6$)$_3$]2.75H$_2$O

Potentiometric titrations of Ni(II) and quinic acid alone were carried out. The titration curves were evaluated with different potential speciation models; mononuclear ([NiLH]$^{2+}$, [NiLH$_{-1}$]$^0$), dinuclear ([Ni$_2$L$_2$H]$^{3+}$) and tetranuclear ([Ni$_4$L$_4$H]$^{5+}$) species emerged in the pH distribution. Moreover, mononuclear [NiL$_3$]$^-$ and [NiL$_3$H$_{-1}$]$^{2-}$ species with a 1:3 Ni:L stoichiometry emerged as representative compounds of the aqueous binary distribution. Of the two species, complex [NiL$_3$]$^-$ reflects the exact nature of the species synthesized and isolated in the solid state (1). That observation projects the complex picture of the aqueous speciation (Figure 2) of the binary Ni(II)-quinic acid.
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Figure 2. Speciation curves of the binary Ni(II) – quinic acid system

Conclusions

The synthesis of 1, its isolation, and spectroscopic characterization provide a clear picture of the structural and chemical interaction of the quinate natural binder with nickel. Moreover, the aqueous speciation of the binary system projects the diversity of species expected to arise as a function of pH and molecular Ni(II):quinate stoichiometry. In so doing, the emerging information leads to a well-defined species distribution of Ni(II) with a low molecular mass ligand, providing further emphasis to the binary and ternary interactions in plant fluids, with any potential activity relating to the physiology or toxic effects in fundamental cell structures.

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