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Journal of Agroalimentary Processes and Technologies 2010, *16* (2), 80-82

*Journal of Agroalimentary Processes and Technologies*

# Structural speciation of Co(II) with hydroxy-carboxylate substrates

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**Received: 20 May 2010; Accepted: 07 June 2010**

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### *Abstract*

The investigation of the pH-dependent synthesis between Co(II) and a hydroxy-carboxylate ligand led to the isolation and characterization of new binary compounds. The new Co(II)-(hydroxy)carboxylate species were synthesized in aqueous solution under various molar ratios and different bases. The compounds were characterized by elemental analysis, spectroscopic techniques (FT-IR, UV-Vis, EPR), magnetic studies, and X-ray crystallography. Potentiometric titrations were also carried out in order to investigate the species distribution as a function of pH. Each new species was shown to contain Co(II) ions in an octahedral environment. The physicochemical profiles of all species, in the solid state and in solution, earmark the importance of aqueous structural speciation, which projects chemical reactivity pathways in the binary Co(II)-quinate system, involving soluble Co(II) forms emerging through interactions with low molecular mass O-containing physiological substrates, such as quinic acid.

***Keywords***: Cobalt(II), (hydroxy)carboxylic acids, potentiometric titrations, X-ray crystallography

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## 1. Introduction

Cobalt is a naturally occurring metal found in rocks, soil, water, as well as in plants and animals. As an essential trace element, cobalt can be involved in biological processes in human physiology. It has been found that cobalt exists in the human body as a metal cofactor, required for a specific group of enzymatic systems ($B_{12}$ coenzyme and vitamin $B_{12}$) [1]. As such, it can coordinate with a number of physiological ligands, low and high molecular mass, including α-hydroxycarboxylic acids and amino acids, entering ternary physiologically important interactions with proteins [2]. Finally, cobalt plays various and important roles in advanced materials.

A representative physiological (hydroxy) carboxylate ligand is the low molecular mass binder D(-)-quinic acid, 1α,3α,4α,5β-tetrahydroxy-1-cyclohexane carboxylic acid. It is a natural molecule, and it can be found in plants, such as cinchona bark, carrots and tobacco leaves [3-5]. It is also known that cyclic polyols (such as D(-)-quinic acid) act as calcium carriers in biological systems. Interest in the employment of quinic acid stems from its use as a versatile chiral starting material in the synthesis of new pharmaceuticals [6]. The herein described work employs quinic acid and explores its chemical reactivity toward Co(II) under pH-specific conditions in the physiological pH range.

## 2. Materials and methods

All manipulations were carried out under aerobic conditions. $Co(NO_3)_2{\cdot}6H_2O$ was purchased from BDH Chemicals, Ltd. $Co(CH_3COO)_2{\cdot}4H_2O$ was purchased from RP Carlo Erba, and D-(-)-quinic acid and $CoCl_2{\cdot}6H_2O$ were purchased from Fluka. Ammonia was purchased from RP Carlo Erba, and ethanol was purchased from PA Panreac.

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KOH and NaOH were supplied by Fluka. Nanopure-quality water was used for all reactions run.

## 3. Results and Discussion

The aqueous synthetic chemistry of the binary system Co(II)-D-(-)-Quinic acid was investigated under specific stoichiometric and pH conditions. As a result, three new species were isolated and characterised. The molecular formula for each species is: $K[Co(C_7H_{11}O_6)_3]\cdot 3C_2H_6O$ (**1**), $Na[Co(C_7H_{11}O_6)_3]\cdot 3C_2H_6O\cdot 2.25H_2O$ (**2**) and $[Co(C_7H_{11}O_6)_2(H_2O)_2]\cdot 3H_2O$ (**3**).

The syntheses of compounds **1-3** were carried out in aqueous media and nanopure water was used for all reactions. The pH was adjusted to 7 with KOH for **1** and to 5.5 with NaOH for **2**. The addition of the bases KOH and NaOH as well as the addition of ethanol were crucial for the isolation of the two distinct Co(II)-quinate species. No base was used for the adjustment of the pH for compound **3**. All three resulting reaction mixtures were placed in the refrigerator at 4 $^{o}$C ultimately leading to crystalline materials.

Elemental analysis pointed to the molecular formulation of compound **1** $C_{27}H_{51}CoKO_{21}$ (M.W. 809.71): Anal. Calcd for **1** C, 40.00; H, 6.30. Found: C, 39.65; H, 6.24; compound **2** $C_{27}H_{55.50}CoNaO_{23.25}$ (M.W. 834.2): Anal. Calcd for **2**: C, 38.87; H, 6.70. Found: C, 38.66; H, 6.53; compound **3** $C_{14}H_{32}CoO_{17}$ (M.W. 531.32) Anal. Calcd for **3** C, 31.16; H, 6.02. Found: C, 31.41; H, 5.91%.

The FT-IR spectra for all the compounds were recorded in KBr and reflected the presence of vibrationally active carboxylate groups. The antisymmetric stretching vibrations $\nu_{as}(COO^-)$ appear around 1625 cm$^{-1}$, whereas the symmetric stretches $\nu_s(COO^-)$ appear in the range 1456 and 1310 cm$^{-1}$ for complex **1**. For complex **2,** the antisymmetric stretching vibrations $\nu_{as}(COO^-)$ appear around 1615 cm$^{-1}$, whereas the symmetric stretches $\nu_s(COO^-)$ appear in the range 1445 και 1323 cm$^{-1}$. For complex **3,** the he antisymmetric stretching vibrations $\nu_{as}(COO^-)$ appear around 1597 cm$^{-1}$, whereas the symmetric stretches $\nu_s(COO^-)$ appear in the range 1452 και 1366 cm$^{-1}$.

The UV/Visible spectra of **1** and **3** were taken in water. Both spectra show a band around $\lambda_{max}$ = 516 nm ($\varepsilon \sim 15$) nm and a distinct shoulder appears around $\lambda = 480$ nm ($\varepsilon \sim 12$).

X-Ray crystallography was instrumental in revealing the three dimensional structure of each investigated molecule. The structure of the anionic complex $[Co(C_7H_{11}O_6)_3]^-$ reveals a mononuclear assembly, in which a Co(II) ion coordinates to three quinic acid ligands in an octahedral environment. The addition of KOH and NaOH, in the case of compound **1** and **2**, was crucial in the investigated reaction because it a) helped to adjust the pH of the reaction mixture, and b) provided the ligands for Co(II) with the appropriate counter ions needed to balance the arisen charge.

The structure of compound $[Co(C_7H_{11}O_6)_2(H_2O)_2]\cdot 3H_2O$ (**3**) reveals a mononuclear assembly different from those in **1** and **2**, where each Co(II) ion coordinates to two quinate ligands in an all oxygen octahedral environment. Finally, quinate binds Co(II) ions through formation of a five-membered metallacyclic ring. The formation of such rings has been already reported in the case of other metal-(hydroxy)carboxylate species.

Beyond analytical, spectroscopic and crystallographic techniques, magnetic susceptibility studies and EPR studies on **1** and **3** were carried out to provide valuable information on the nature of each species both in the solid state and in solution. To this end, aqueous speciation studies of the binary system of Co(II)-quinic acid were investigated in order to shed light into the different chemical aspects arising from varying metal-ligand stoichiometries and pH values.

## 4. Conclusion

In the aforementioned work, the aqueous synthetic chemistry of Co(II) toward D-(-)-quinic acid was investigated in-depth, in an effort to delineate the interactions of the divalent metal ion with a (hydroxy)carboxylate substrate in aqueous solutions leading to isolable crystalline materials. Therefore, reactions were carried out between Co(II) ions and quinic acid. The synthetic efforts led to the isolation of discrete soluble and potentially bioavailable species under variable stoichiometries, pH values and different bases. The solid-state structures and solution physicochemical properties of the arisen species reflect the notion that Co(II) is a metal ion capable of coordinating variable nature biotargets, a) entering physiologically important binary and ternary interactions, and b) leading to discrete species of specific chemical reactivity.

## Acknowledgements

The authors would like to acknowledge the financial support to this project by a ‘‘PENED” grant co-financed by the E.U.-European Social Fund (75%) and the Greek Ministry of Development-GSRT (25%).

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