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# SYNTHESIS AND CHARACTERIZATION OF TWO NEW Co(II)-QUINATE COMPLEX FORMS FROM AQUEOUS SOLUTIONS. CORRELATION WITH THE BIOLOGICAL Co(II) SPECIATION

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## Abstract

*Two new Co(II)-quinate species were synthesized in aqueous solution at the optimum pH 5. They were isolated in a pure crystalline form and were characterized by elemental analysis, spectroscopic techniques (FT-IR, UV-Vis, EPR), magnetic studies and X-ray crystallography. The two new isostructural species contain cobalt ions in an octahedral environment, and each cobalt ion coordinates with three quinic acids.*

***Keywords**: Cobalt(II), D-(-)-Quinic acid, binary interactions, aqueous speciation*

## Introduction

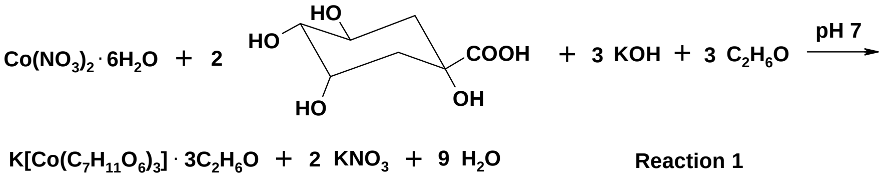
Cobalt is an essential trace metal ion, which is involved, in key biomolecules in human physiology. As an abundant metalloelement, cobalt can also play various roles in advanced materials. Cobalt has been found to exist in the human body as a metal cofactor, required for a specific group of enzymatic systems such as the $B_{12}$ coenzyme and vitamin $B_{12}$ (Hamilton, 1987). Cobalt(II) is a metal ion capable of coordinating with ligands like α-hydroxycarboxylic acids or carboxylic acids, entering physiologically important binary and ternary interactions such as proteins (Dickinson, 1973).

One such representative acid is the low molecular mass binder D(-)-quinic acid, 1α,3α,4α,5β-tetrahydroxy-1-cyclohexane carboxylic acid. D(-)-quinic acid, as a natural molecule, can be found in plants, like carrots and tobacco leaves (Bohm, 1965; Corse, 1966; Kelley, 1976). It is known that cyclic polyols 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 Co(II). To this end, investigating the aqueous interactions of Co(II) with quinic acid was the crux of the efforts aiming at comprehending the intricate role the metal ion plays in natural biological systems

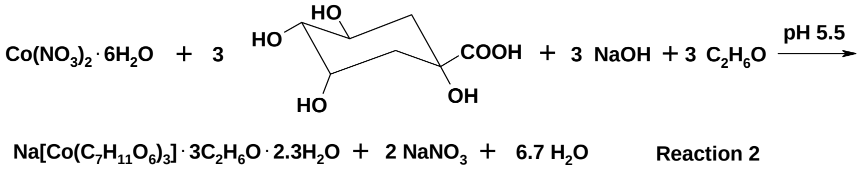
## Experimental

We investigated the aqueous synthetic chemistry of the binary system Co(II)-D-(-)-Quinic acid. There, under specific stoichiometric conditions and numerous reactions, the arisen reactivity led to the isolation of two new species $K[Co(C_7H_{11}O_6)_3] \cdot 3C_2H_6O$ (**1**), $Na[Co(C_7H_{11}O_6)_3] \cdot 3C_2H_6O \cdot 2.3H_2O$ (**2**).

More specifically, the synthesis of **1** and **2** were carried out in aqueous media (nanopure water was used for all reactions). The pH was adjusted to 7 with KOH for complex **1** and to 5.5 with NaOH for complex **2**. The addition of the bases KOH and NaOH as well as the addition of ethanol were crucial for the isolation of the two isostructural species. The resulting reaction mixtures were placed in the refrigerator at 4 $^{o}$C. The stoichiometric reactions for the synthesis of complexes 1 and 2 are given below:



Reaction 1



Reaction 2

Elemental analysis pointed to the molecular formulation of complex **1**. $C_{27}H_{51}CoKO_{21}$ (M.B. 809.71) Anal. Calcd for **1**: C, 40.00; H, 6.30: Found: C, 38.19; H, 5.93%. Elemental analysis pointed to the molecular formulation of complex **2**. $C_{27}H_{55.50}CoNaO_{23.25}$

(M.B.834.13) Anal. Calcd for **2**: C, 38.84; H, 6.65. Found: C, 37.66; H, 6.13 %. Complexes **1** and **2** were further characterized by FT-IR and X-Ray crystallography on isolated single crystals from the reaction mixture.

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

The UV/Visible spectrum of **1** was taken in water (Figure 1). The spectrum shows a band around $\lambda_{max}$ 516 nm ($\varepsilon$ ~ 15) nm. Also, a distinct shoulder appears around $\lambda$ 480 nm ($\varepsilon$ ~12).

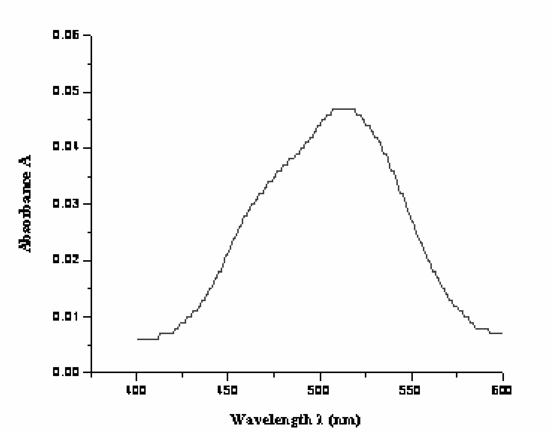


**Figure 1.** The UV/Visible spectra of the $[Co(C_7H_{11}O_6)_3]^-$

X-Ray crystallography was instrumental in revealing the three dimensional structure of the investigated molecules. The structure of complex $[Co(C_7H_{11}O_6)_3]^-$ is presented in Figure 2. Each Co(II) ion coordinates to three quinic acids in an octahedral environment. The addition of KOH and NaOH, as bases, was crucial in the investigated reaction. Not only did that help adjust the pH of the reaction mixture, but also provided the ligands for Co(II) with the appropriate counter ions needed to balance the arisen charge of the assembled anionic species.

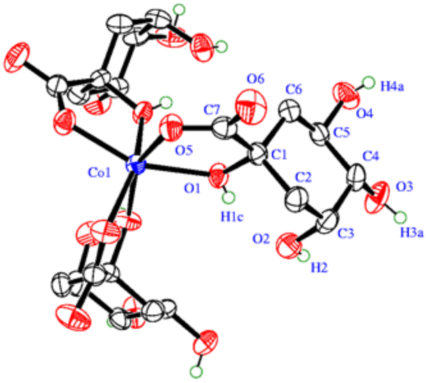


**Figure 2.** ORTEB diagram of the anionic complex $[Co(C_7H_{11}O_6)_3]^-$

Moreover, magnetic susceptibility studies and EPR studies on **1** and **2** were carried out to provide valuable information on the nature of each species both in the solid state and in solution. Finally, speciation studies of the binary system of Co(II)-quinic acid were carried out to shed light into the different chemical aspects arising from varying Co(II)-substrate stoichiometries and pH values.

## Conclusions

From the collective study conducted here, the aqueous chemistry of Co(II) was examined in-depth, targeting its interactions with organic substrates in aqueous solutions. Cobalt(II) is a metal ion capable of coordinating to biotargets entering physiologically important binary and ternary interactions. To this end, reactions were carried out between Co(II) and the α-hydroxycarboxylic acid quinic acid. These efforts led to the isolation of the first soluble bioavailable species between Co(II) and quinic acid under variable stoichiometries, pH values and bases. The physicochemical properties of these species denote their structural and chemical reactivity characteristics that render them competent components of aqueous speciation distributions of biological relevance.

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