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Investigation of Co(II)-hydroxycarboxylate interactions in aqueous solutions

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Abstract

The chemical reactions of Co(II) and D(-)-quinic acid led to the isolation of three new crystal structures. The new Co(II)-quinate species were synthesized in aqueous solution under different molar ratios. They were characterized by elemental analysis, spectroscopic techniques (FT-IR, UV-Vis, EPR), magnetic studies and X-ray crystallography. Moreover, potentiometric titrations were carried out. Each new species contains cobalt ions in an octahedral environment.

Keywords: Cobalt(II), D-(-)-Quinic acid, potentiometric titrations

1. Introduction

Cobalt is a naturally occurring element found in rocks, soil, water, plants, and animals. As an essential trace metal ion, cobalt can be involved in biological processes in human physiology. Moreover, 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} [1]. Cobalt can coordinate with a number of physiological ligands (both low and high molecular mass), such as α-hydroxycarboxylic acids, carboxylic acids or amino acids, entering physiologically important interactions with proteins [2].

One such representative physiological ligand is the low molecular mass binder D(-)-quinic acid, 1α,3α,4α,5β-tetrahydroxy-1-cyclohexane carboxylic acid.

D(-)-quinic acid is a natural molecule, which can be found in plants, like cinchona bark, carrots and tobacco leaves [3-5].

It is 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 is a versatile chiral starting material in the synthesis of new pharmaceuticals [6]. The herein described work employs quinic acid and explores its chemical reactivity with the essential metal ion Co(II) under pH specific conditions in the physiological pH range.

2. Experimental Section

The aqueous synthetic chemistry of the binary system Co(II)-D-(-)-Quinic acid was investigated. Under specific stoichiometric and pH conditions, the binary synthetic system was investigated, giving rise to three new species were isolated. The molecular formula for each species is: $K[Co(C_7H_{11}O_6)_3]\cdot 3C_2H_6O$ (**1**), $Na[Co(C_7H_{11}O_6)_3]\cdot 3C_2H_6O\cdot 2.3H_2O$ (**2**) and $[Co(C_7H_{11}O_6)_2(H_2O)_2]\cdot 2H_2O$ (**3**).
More specifically, the synthesis of **1, 2** and **3** 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**.

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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. On the other hand, no base was used for the adjustment of the pH for complex **3**. The resulting reaction mixtures were placed in the refrigerator at 4 °C.

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 %. Elemental analysis pointed to the molecular formulation of complex **3** $C_{14}H_{32}CoO_{17}$ (M.B. 531.32): C, 31.16; H, 6.02. Found: C, 32.41; H, 5.91 %.

The FT-IR spectra for all the complexes 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**. 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 **2**. The 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} for complex **3**.

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

X-Ray crystallography was instrumental in revealing the three dimensional structure of the investigated molecules.

The structure of complex $[Co(C_7H_{11}O_6)_3]^-$ 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, as bases, was crucial in the investigated reaction. Not only does that help adjust the pH of the reaction mixture, but also provides the ligands for Co(II) with the appropriate counter ions needed to balance the arisen charge same as the addition of ethanol.

The structure of complex $[Co(C_7H_{11}O_6)_2(H_2O)_2] \cdot 3H_2O$ reveals another mononuclear assembly, in which each Co(II) ion coordinates to two quinic acid ligands in an octahedral environment. In each case, quinate binds to Co(II) through formation of a five-membered metallacyclic ring, making the arising species quite stable.

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. Finally, 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 Co(II)-substrate stoichiometries and pH values.

3. Conclusions

In this work, the aqueous synthetic chemistry of Co(II) toward quinic acid was investigated in-depth, in an effort to comprehend the interaction of that metal ion with organic substrates in aqueous solutions. To this end, reactions were carried out between Co(II) and the above physiological α-hydroxycarboxylic acid. The synthetic efforts led to the isolation of discrete soluble and potentially bioavailable species between Co(II) and quinic acid under variable stoichiometries, pH values and bases. The solid-state structures and solution physicochemical properties of the arisen species reflect the notion that cobalt is a metal ion capable of coordinating with biotargets entering physiologically important binary and ternary interactions.

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