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The formation of Ca(II) enolato complexes with α - and β -ketoglutarate in strongly alkaline solutions

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ABSTRACT

In the present study the proton dissociation and calcium complex formation of α - and β -ketoglutarate (2- and 3-oxopentane-dioate, α -Ket²⁻ and β -Ket²⁻, respectively) in neutral and alkaline aqueous solutions was explored. From potentiometric measurements, the equilibrium constants of the $[\text{Ca}(\alpha\text{-Ket})]^0$ and $[\text{Ca}(\beta\text{-Ket})]^0$ complexes formed in neutral medium were determined to be $\log K_{1,1}^\alpha = 1.15 \pm 0.02$ and $\log K_{1,1}^\beta = 0.78 \pm 0.02$, respectively. In alkaline medium, it was found for both ligands that the methylene group underwent deprotonation yielding the carbanion-enolate anion. The deprotonation constants, $\text{p}K_a^\alpha$ and $\text{p}K_a^\beta$, were found to be 15.16 ± 0.01 and 14.41 ± 0.01 , respectively. The calcium complexing behaviour of the two ligands was also studied in strongly alkaline medium. Under these conditions, the Ca^{2+} ion was capable of promoting the deprotonation of the ligands and forming various enolato-type complexes. The formation of both mono- and binuclear species were deduced, their formulae are suggested to be $[\text{Ca}(\alpha\text{-Ket})\text{H}_{-1}]^-$, $[\text{Ca}_2(\alpha\text{-Ket})\text{H}_{-3}]^-$, $[\text{Ca}(\beta\text{-Ket})\text{H}_{-1}]^-$, $[\text{Ca}_2(\beta\text{-Ket})\text{H}_{-1}]^+$ with the formation constants of $\log \beta_{1,1,-1}^\alpha = -11.91 \pm 0.02$, $\log \beta_{2,1,-3}^\alpha = -36.10 \pm 0.06$, $\log \beta_{1,1,-1}^\beta = -11.58 \pm 0.01$, $\log \beta_{2,1,-1}^\beta = -10.80 \pm 0.03$, respectively. Beside the formation of the rare Ca^{2+} -enolato complexes, the deprotonation of the hydrating water molecules around the Ca^{2+} ion was also invoked in some cases.

1. INTRODUCTION

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