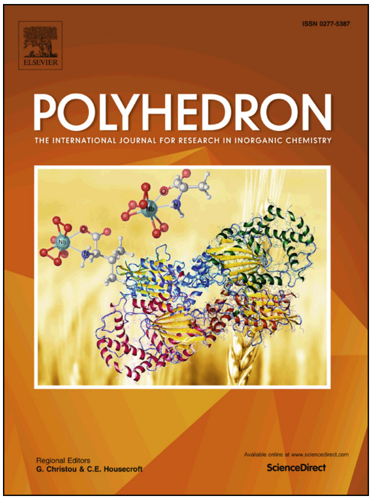

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The formation of Ca(II) enolato complexes with α- and β-ketoglutarate in strongly alkaline solutions

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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, $\alpha\text{-Ket}^{2-}$ and $\beta\text{-Ket}^{2-}$, respectively) in neutral and alkaline aqueous solutions was explored. From potentiometric measurements, the equilibrium constants of the $[Ca(\alpha\text{-Ket})]^0$ and $[Ca(\beta\text{-Ket})]^0$ 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, pK_a^{α} and pK_a^{β}, 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 $[Ca(\alpha\text{-Ket})H_{-1}]^-$, $[Ca_2(\alpha\text{-Ket})H_{-3}]^-$, $[Ca(\beta\text{-Ket})H_{-1}]^-$, $[Ca_2(\beta\text{-Ket})H_{-1}]^+$ 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