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# CONTROLLED COMPLEXATION OF Zr(IV) AND Hf(IV) WITH AMINO-DERIVATIVES OF 2,6-PYRIDINEDICARBOXYLATES: A COMPUTATIONAL APPROACH FOR SEPARATION EFFICIENCY ENHANCEMENT

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Extraction of ultra-pure zirconium and hafnium would be a value addition to the zircon ($ZrSiO_4$) ore available in Sri Lanka. However, extracting the ultra-pure Zr and Hf has become impossible to countries such as Sri Lanka due to the complexity, environmental impact and the cost of the currently available methods. Among them, fractional crystallisation is the simplest method with the least environmental impact, although its separation efficiency is low. In this study, a theoretical approach was taken to improve the separation efficiency of fractional crystallisation through complex formation with 2,6-pyridinedicarboxylate (PDA). Initially, the reaction energy for each ligation step during the formation of $[M(PDA)_3]^{2-}$ starting from $[M(H_2O)_9]^{4+}$ was calculated with density functional theory (DFT) using ORCA 5.0. However, based on the calculated reaction energies, it was not possible to separate Zr(IV) and Hf(IV) with the formation of $[M(PDA)_3]^{2-}$, due to similar reaction energies in the latter steps. However, in the initial step, there is a significant difference between Zr(IV) and Hf(IV) complex formations. Consequently, calculations were extended to determine the reaction energies with amino derivatives of PDA for the initial step. If one of the metals shows significant favorability to ligate with a particular amino derivative, it is possible to stoichiometrically drive the ligation toward a particular metal ion. Thereafter, the remaining complex substitutions can be performed with 2,6-PDA, leading to complexes with differing physical properties. The calculations, performed at the hybrid B3LYP functional, and def2-TZVP basis set, accounting for the basis-set superposition error, indicate that 4-amino-PDA show the highest favorability to ligate with Zr(IV) in the initial step among other amino derivatives of PDA. Therefore, it is possible to crystallize $[Hf(PDA)_3]^{2-}$, if a controlled amount of 4-amino-PDA is used in the initial step. It is expected that properties of dipole-moment and solubility be significantly different for the two complexes, allowing easier and more efficient separation.

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