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COMPUTATIONAL STUDIES ON STABILITY OF EIGHT COORDINATED COMPLEXES FORMED BY Zr(IV) AND Hf(IV) WITH BIDENTATE LIGANDS

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Extracting ultra-pure forms of either Zr or Hf is challenging due to the coexistence of Zr(IV) and Hf(IV) in their natural source of minerals and their similar chemical properties. In a mixed ligand environment, Zr(IV) and Hf(IV) can form complexes with different combinations of ligands with significant stability differences. If the ligand combination of the most stable complex formed by Zr(IV) or Hf(IV) differs from the other, it is possible to separate Zr(IV) and Hf(IV) through selective precipitation or fractional crystallization. Hence, developing an environmentally friendly, efficient and cost-effective separation method is possible. In this study, density functional theory (DFT) calculations were carried out to find suitable mixed bidentate-ligand systems to separate Zr(IV) and Hf(IV). According to the initial DFT calculations on the stability of possible eight coordinate complexes formed by Zr(IV) and Hf(IV) with commonly available bidentate ligands; acetylacetonate (acac), glycine (gly), malonate (mal) and oxalate (ox), Zr(IV) complexes are more stable than Hf(IV), for all except acac complexes. The stability of possible mixed ligand complexes formed by Zr(IV) and Hf(IV) with different ratios of acac (primary ligand) and other bidentate ligands (secondary ligands) were calculated. Based on the calculations, the most stable complexes for acac-ox mixed ligand systems are $[Zr(ox)_4]^{4-}$ and $[Hf(ox)_4]^{4-}$, and for acac-mal combinations, are $[Zr(mal)_4]^{4-}$ and $[Hf(mal)_4]^{4-}$. However, for an acac-gly system, the most stable complex for Hf(IV) is $[Hf(acac)_4]$, while for Zr(IV), $[Zr(acac)_4]$ is the least stable complex. The most stable complex for Zr(IV) is $[Zr(acac)(gly)_3]$. The calculated stability data indicates that in an acac-gly system, Zr(IV) shows preferential ligation of gly while Hf(IV) prefers acac, which may allow for the development of efficient and environmentally friendly separation process for the production of ultra-pure forms of Zr and Hf from the zircon deposits available in Sri Lanka in the future.

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