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Thermodynamics of HOPO Coordination with Lanthanide Series

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Rare-earth elements (REEs), composed of fifteen lanthanides from ^{57}La to ^{71}Lu in addition to ^{21}Sc and ^{39}Y, possess unique physical and chemical properties and are integral for a variety of technology applications, ranging from energy generation to high-tech industry. Liquid−liquid separation is accepted as the most appropriate technology to individually recover REEs and offers a continuous operation and substantial production capacity[1]. The hydroxypyridinone (HOPO) chelator has high metal-binding selectivity and applicability because it exhibits a unique combination of properties interesting in separation processes, such as: (i) water solubility, (ii) structures consisting solely of H, C, N, and O atoms, (iii) ability to control metal oxidation states without additional redox-active species, (iv) extremely high charge-based selectivity, and (v) high stability of metal-ligand complexes even in strong acids[2].

The geometries were optimized using the PBE and M06 functional, employing the def2-TZVP basis sets. For rare earth elements (REE), the inner core electrons have been replaced by effective potentials (def2-ECP). The influence of the solvent environment, was considered, using (SMD). All calculations were performed using ORCA 5.0.4[3].

In our investigation, we assessed the HOPO coordination with Rare Earth Elements (REE), especially with La, Ce, Nd, Er, Yb, and Lu. The HOPO is octadentate ligand which fits well with usual coordination number of the light REE such as Er, Yb and Lu. For the La, Ce and Nd the usual coordination number is 9, therefore, a water molecule was added in the coordination sphere.

The thermodynamic analysis of the complex formation provides valuable insights into the intricacies of REE separation. The factors that govern the stability of the coordination toward the heavy REE with respect to the light ones are revealed. The formation free energies of the HOPO coordination are compared to the available experimental data.

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