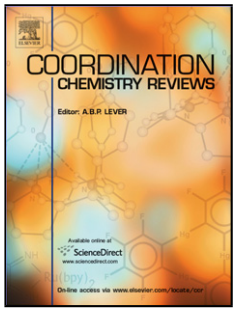

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The Electrochemical Behavior of Cerium(III/IV) Complexes: Thermodynamics, Kinetics and Applications in Synthesis

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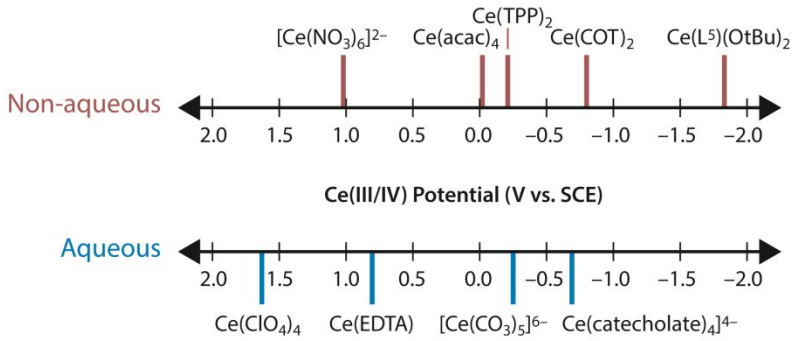
Abstract

A key characteristic of the element cerium is its reversible redox chemistry between trivalent and tetravalent forms, which is central to the application of cerium in synthetic and materials chemistry. Herein we survey the general thermodynamic and kinetic characteristics and reported potentials for molecular cerium redox chemistry. The collected data illustrate that the local electronic environment provided by the coordination sphere around a cerium ion has a great effect on the oxidizing ability of the ion. The survey also illustrates the ligand types that most effectively stabilize each oxidation state. We expect the collection and comparison of these data will facilitate the development of new cerium(IV) chemistry and applications in oxidation and reduction chemistry.



Keywords: lanthanides; cerium; electrochemistry; electron transfer; oxidation

Abbreviations: acac, acetylacetonate; BINOL, 1,1'-bi-2-napthol; Bu, butyl; BQ, benzoquinone; CAN, ceric ammonium nitrate; CV, cyclic voltammetry/voltammagram; CMPO, *n*-octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide; Cp, cyclopentadienyl; dap, diazaporphyrin; DMSO, dimethylsulfoxide; DPA, dipicolinic acid; DTPA, diethylenetriaminepentaacetic acid; EDTA, ethylenediaminetetraacetic acid; E_{pa}, electrochemical potential at peak anodic current; E_{pc}, electrochemical potential at peak cathodic current; Et, ethyl; Fc, ferrocene; H6TrenSal, tris((2-hydroxybenzyl)aminoethyl)amine; HBP, hexadecahydrotetrabenzoporphyrin; HOPO, hydroxypyridinone; IL, ionic liquid; ^{i}Pr, *iso*-propyl; irr, irreversible; MBP, 2,2'-methylenebis(6-*tert*-butyl-4-methylphenolate); Me, methyl; Me-3,2-HOPO, 1-methyl-3-hydroxy-2(*1H*)-