

# EFFECT OF REDOX INACTIVE METAL ION–NICKEL(III) INTERACTION ON THE REDOX PROPERTIES AND PROTON–COUPLED ELECTRON TRANSFER REACTIVITY

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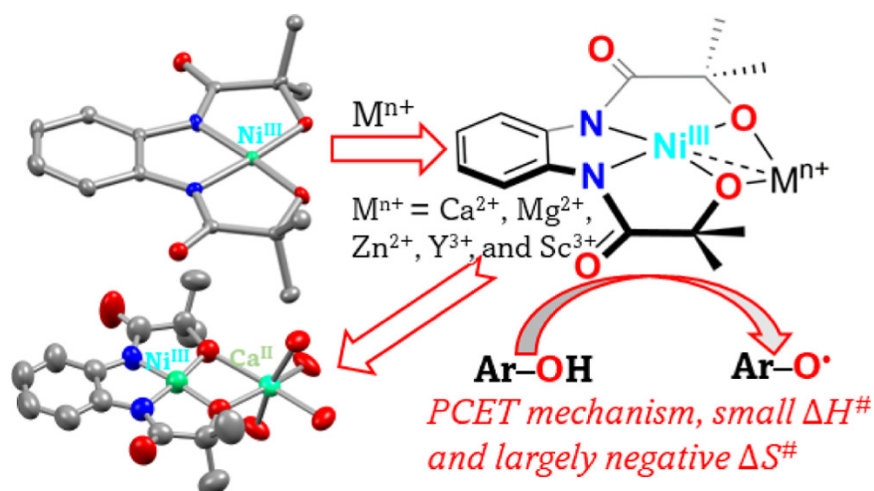
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High-valent nickel species are frequently invoked as key intermediates in the catalytic cycle of different enzymatic systems like [NiFe]-hydrogenase, and Ni superoxide dismutase (NiSOD).<sup>1</sup> Also, the coordination of Lewis acid (LA) at the secondary coordination sphere of the redox-active cofactor has an enormous effect on the reactivity.<sup>2</sup> In this regard, a mononuclear nickel(II) and nickel(III) complexes of a bis-amidate-bis-alkoxide ligand, (NMe<sub>4</sub>)<sub>2</sub>[Ni<sup>II</sup>(HMPAB)] (1) and (NMe<sub>4</sub>)[Ni<sup>III</sup>(HMPAB)] (2), has been isolated and characterized respectively. The reaction of redox-inactive metal ions (M<sup>n+</sup> = Ca<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>, Y<sup>3+</sup>, and Sc<sup>3+</sup>) with 2 resulted in 2-M<sup>n+</sup> adducts, which was assessed by an array of spectroscopic techniques. The X-ray structure of Ca<sup>2+</sup> coordinated to Ni(III) complexes, 2-Ca<sup>2+</sup>T, was determined and exhibited an average Ni–Ca distance of 3.1253 Å, close to the metal ions' covalent radius. Further, the reactivity studies of 2 and 2-M<sup>n+</sup> with different 4-X-2,6-di-*tert*-butylphenol (4-X-DTBP) and other phenol derivatives were performed, and a proton-coupled electron transfer (PCET) mechanism was observed based on in-depth kinetic analysis. The second-order rate constant (*k*<sub>2</sub>) values of 2-M<sup>n+</sup> species with 4-OMe-2,6-DTBP increases with increasing the Lewis acidity of redox-inactive metal ions. Our findings show the significance of the secondary coordination sphere effect on the PCET reactivity of metal complexes.



[1] Barondeau, D. P.; Kassmann, C. J.; Bruns, C. K.; Tainer, J. A.; Getzoff, E. D.; *Biochemistry*, 2004, 43, 8038-8042.

[2] Boussac, A.; Rutherford, A. W.; *Biochemistry* 1988, 27, 3476-3483.