

# Role of Redox-Inactive Metal Ions in Modulating the Reduction Potential of Uranyl Schiff Base Complexes: Detailed Experimental and Theoretical Studies

Tanmoy Kumar Ghosh, Souvik Maity, Soumavo Ghosh, Rosa M. Gomila, Antonio Frontera,\* and Ashutosh Ghosh\*



Cite This: *Inorg. Chem.* 2022, 61, 7130–7142



Read Online

ACCESS |



Metrics & More

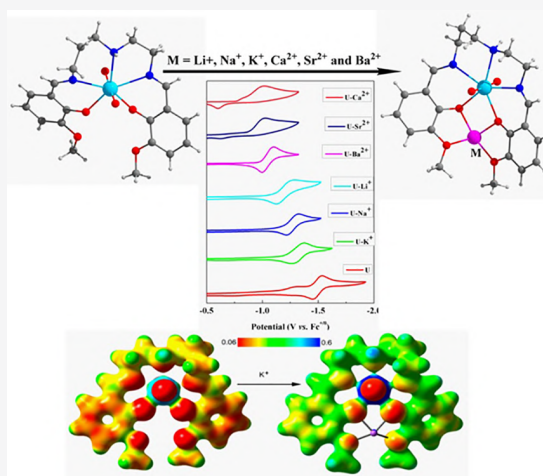


Article Recommendations



Supporting Information

**ABSTRACT:** A mononuclear uranyl complex,  $[\text{UO}_2\text{L}]$  (1), has been synthesized with the ligand  $N,N'$ -bis(3-methoxy-2-hydroxybenzylidene)-1,6-diamino-3-azahexane ( $\text{H}_2\text{L}$ ). The complex showed a reversible U(VI)/U(V) redox couple in cyclic voltammetric measurements. The reduction potential of this couple showed a positive shift upon the addition of redox-inactive alkali- and alkaline-earth Lewis acidic metal ions ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$ ) to an acetonitrile solution of complex 1. The positive shift of the reduction potential has been explained on the basis of the Lewis acidity and internal electric-field effect of the respective metal ions. The bimetallic complexes  $[\text{UO}_2\text{LLi}(\text{NO}_3)]$  (2),  $[\text{UO}_2\text{LNa}(\text{BF}_4)]_2$  (3),  $[\text{UO}_2\text{LK}(\text{PF}_6)]_2$  (4),  $[(\text{UO}_2\text{L})_2\text{Ca}] \cdot (\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$  (5),  $[(\text{UO}_2\text{L})_2\text{Sr}(\text{H}_2\text{O})_2] \cdot (\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$  (6), and  $[(\text{UO}_2\text{L})_2\text{Ba}(\text{ClO}_4)] \cdot (\text{ClO}_4)$  (7) have also been isolated in the solid state by reacting complex 1 with the corresponding metal ions and characterized by single-crystal X-ray diffraction. Density functional theory calculations of the optimized  $[\text{UO}_2\text{LM}]^{n+}$  complexes have been used to rationalize the experimental reduction and electric-field potentials imposed by the non-redox-active cations.



## INTRODUCTION

Redox-inactive metal ions that act as Lewis acids are often used in combination with redox-active transition-metal complexes to influence a variety of chemical transformations such as oxygen atom transfer, oxygen reduction reactions, olefin hydrogenation, polymerization, coupling reactions, etc.<sup>1–6</sup> In addition, such metal ions play a crucial role in nonbiological electron-transfer reactions such as water oxidation catalyzed by various heterometallic transition-metal complexes and also in the control of biological electron-transfer processes.<sup>7–10</sup> For example, during oxygen evolution by oxidation of water in photosystem II, the presence of a  $\text{Ca}^{2+}$  ion is essential for activity in the oxygen-evolving complex.<sup>11,12</sup> Among the various Lewis acidic cations having sizes similar to that of the  $\text{Ca}^{2+}$  ion [e.g.,  $\text{Sr}(\text{II})$ ,  $\text{Cd}(\text{II})$ , etc.] or stronger Lewis acidity ( $\text{Mg}^{2+}$  and  $\text{La}^{3+}$  ions) than  $\text{Ca}^{2+}$  ion, only  $\text{Sr}^{2+}$ -substituted photosystem II was found to be active for oxygen evolution.<sup>9,13–16</sup> These observations suggest that the unique combination of size and Lewis acidity of the metal ions has a pivotal role for their reactivity.<sup>14</sup> Considering these two crucial factors, several groups have synthesized various bimetallic transition-metal complexes with Lewis acidic cations and studied their electrochemical properties in order to correlate

the redox potential of the synthesized complexes with the Lewis acidity of the corresponding redox-inactive metal ions.<sup>4,17–21</sup> The shift of the redox potential of the bimetallic complexes is dependent on the electron-withdrawing capability of the proximal redox-inactive metal ions because they affect the electronic structures of the molecules to different extents. Like the size and Lewis acidity of the proximal metal ions, its intramolecular field effect can also play an important role in both modulating the electronic structure and shifting the redox potential.<sup>22–24</sup> However, this field effect has been explored only in a few transition-metal complexes, and no report of this effect on the redox potential of U has been found in the literature to date.

N and O donor Schiff base ligands have attracted significant attention in the field of coordination chemistry of inner

Received: February 25, 2022

Published: April 25, 2022

