

# En Route Activity of Hydration Water Allied with Uranyl ( $\text{UO}_2^{2+}$ ) Salts Amid Complexation Reactions with an Organothio-Based (O, N, S) Donor Base

Jagriti Singh, Dolly Yadav, and Jai Deo Singh\*<sup>✉</sup>

Department of Chemistry, Indian Institute of Technology Delhi (IITD), Hauz Khas, New Delhi 110 016, India

## Supporting Information



**ABSTRACT:** This study provides en route activity of hydration water allied with uranyl salts amid complexation reactions with a donor species  $L$  bearing O, N, and S (phenolic,  $-\text{OH}$ ; imine,  $-\text{HC}=\text{N}-$ ; and thio-,  $-\text{S}-$ ) donor functionalities. The  $\text{UO}_2^{2+}/L$  reaction encounters a series of hydrolytic steps with hydration water released from uranyl salts during the complexation processes. Primarily, the coordinated  $[\text{L}_{(-\text{HC}=\text{N})(\text{OH})(-\text{HC}=\text{N})}] \rightarrow \text{UO}_2(\text{NO}_3)_2/(\text{OAc})_2$  species formed during the complexation process undergoes partial hydrolysis of the coordinated ligand resulting in the isolation of an aldehyde coordinated uranyl species  $[\text{L}_{(-\text{HC}=\text{N})(\text{OH})(-\text{HC}=\text{O})}] \rightarrow \text{UO}_2(\text{NO}_3)_2/(\text{OAc})_2$ . The influence of hydration water continued as the reaction further proceeded to the next stage resulting in alteration of the aldehyde coordinated uranyl species  $[\text{L}_{(-\text{HC}=\text{N})(\text{OH})(-\text{HC}=\text{O})}] \rightarrow \text{UO}_2(\text{NO}_3)_2/(\text{OAc})_2$  to an oxidized carboxy coordinated uranyl species  $[\text{L}_{(-\text{HC}=\text{N})(\text{OH})(-\text{C}(=\text{O})\text{O})}] \rightarrow (\text{NO}_3)/(\text{OAc})_2$  without the use of any external oxidizing agents. These studies are of particular significance as they allow one to realize the adventitious role of hydration water released from commonly used uranyl salts during their reaction with organic donor substrates in nonaqueous medium. These results also form an experimental basis to understand the critical behavior of  $\text{UO}_2^{2+}$  ion activity (as oxidizing, reducing, or catalytic) relevant in many chemical, biological, and environmental processes.

## INTRODUCTION

An understanding of the behavior of the  $\text{UO}_2^{2+}$  ion among the actinides has been the subject of particular attention due to increasing global nuclear energy demand.<sup>1</sup> As a consequence, their presence in nature also poses serious environmental concerns where they may come across a myriad of chemical, geochemical, biochemical, and environmental processes.<sup>2</sup> Naturally, the knowledge of the behavior of cationic  $\text{UO}_2^{2+}$  is a prerequisite for a precise monitoring, speciation, and furthermore their interactions during migration within terrestrial humic substances.<sup>3</sup> Basically, humic substances have been considered as possible remediation strategies in safe nuclear waste alteration and reprocessing of nuclear fuel sources.<sup>4</sup> Although the interactive behavior of the  $\text{UO}_2^{2+}$  ion toward humic substances is well documented, uncertainties remain due to the structural complexities that vary as a function of pH or as a function of metal ion concentration.<sup>5</sup> Similarly, intricate reaction dynamics of the  $\text{UO}_2^{2+}$  ion that normally go by an oxidative–reductive process in aqueous or

organic solutions result in structural diversities, and therefore, there is always uncertainty in their actual speciation and geochemical migration. For example,  $\text{U(VI)}$  has a strong tendency to hydrolyze and support a range of oxo- and hydroxo- species ( $m\text{UO}_2^{2+} + n\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_m(\text{OH})_n^{(2m-n)+} + n\text{H}^+$ , where the  $n$  and  $m$  range is 1–5 or 1–9) in aqueous medium.<sup>6</sup> There is also a bias to the hydrolysis reaction of the  $\text{UO}_2^{2+}$  ion in different environments (acidic or basic conditions as well as aerobic and anaerobic environments) as  $\text{H}^+$  and  $\text{OH}^-$  ions are freed from hydrolytic activity of  $\text{UO}_2^{2+}$  ion through their biotic and abiotic interactions. This further leads to substantial uncertainties about speciation of the uranyl ion in a similar environment as different species and several coexisting polymeric species at similar concentration and pH range may be produced.<sup>7</sup> Nevertheless, an understanding of the behavior of the  $\text{UO}_2^{2+}$  ion in diverse environments is

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