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A DFT Study on Uranyl Complexation with Pyridine-3-carboxylic Acid in Aqueous Solution

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1. Introduction

Understanding the geochemical behavior of uranium(VI), which occurs in aqueous solutions as uranyl species (UO_2^{2+} and its complexes), is critical for assessing its mobility at contaminated sites and within radioactive waste disposal systems. Uranium(VI) speciation in natural waters is highly sensitive to the presence of natural organic matter (NOM), which contains a diverse array of functional groups capable of forming stable complexes with cations [1–5]. Among these, nitrogen-containing heteroaromatic carboxylates constitute a non-negligible fraction of NOM and can provide energetically favorable coordination for the uranyl moiety [6–8]. In particular, pyridine-3-carboxylic acid (nicotinic acid) has been adopted as one of the representative model ligands of NOM to elucidate the structure and thermodynamics of uranyl complexation [7]. Its structure, featuring both a pyridine and a carboxyl group, enables systematic investigation of the structural and electronic effects of mixed N- and O-donor sites on uranyl coordination. Despite the potential influence of such heterocyclic motifs on uranium(VI) speciation, their thermodynamic properties and pH-dependent stability remain insufficiently explored. Experimental determination of stability constants for these uranyl complexes is often challenging, particularly when it comes to resolving the protonation states of functional groups that are not directly involved in the coordination. In this context, density functional theory (DFT) provides a powerful complementary approach by offering access to electronic structure information and enabling the prediction of thermodynamic parameters, thereby facilitating the resolution of such ambiguities. Here, we employ ωB97X hybrid functional to optimize geometries and compute Gibbs free energies for a series of uranyl–nicotinate species, with the specific aim of quantifying the acid dissociation constant (pK_a) of pyridine nitrogen when the ligand's carboxyl group forms a bidentate chelate with uranyl in aqueous solution. By clarifying the structural stability and pH-dependent speciation of these complexes, this study contributes to reducing uncertainties in thermodynamic descriptions of interactions between uranyl and NOM. Collectively, these findings are expected to strengthen the reliability of geochemical models used to predict the migration of uranium(VI) in complex environmental systems.

2. Computational methods

All DFT calculations were performed using the ORCA quantum chemistry program package [9]. Geometry optimizations and subsequent harmonic vibrational frequency calculations were carried out using the ωB97X hybrid functional augmented with Grimme's D4 dispersion correction. Scalar relativistic effects were treated with the zeroth-order regular approximation (ZORA). The all-electron relativistic SARC-ZORA-TZVP basis set was employed for uranium, while the ZORA-def2-TZVP basis set was used for light atoms (C, H, O, and N). The RIJCOSX approximation was applied to accelerate the evaluation of exact exchange, together with the corresponding auxiliary basis sets (SARC/J for uranium and def2/J for light atoms). To accurately simulate the aqueous environment, a cluster-continuum approach was adopted. Explicit water molecules were included to describe first-shell hydration in the uranyl equatorial plane and local hydrogen-bonding network near the pyridine moiety, and bulk solvation was accounted for using the SMD model. Vibrational frequency analyses were performed to verify that all optimized structures correspond to true local minima (no imaginary frequencies) and to obtain thermal corrections to 298.15 K and 1 atm. To improve the accuracy of evaluated thermodynamic parameters and to avoid uncertainties associated with direct calculation of proton solvation free energies, a proton-exchange reaction scheme was employed. Specifically, the Gibbs free energy change (ΔG) for an isodesmic proton transfer reaction between the protonated uranyl-nicotinate complex and the free nicotinate ligand was computed (see eq. (1)). The pK_a of pyridine nitrogen in the complex was then obtained by anchoring the computed ΔG to the experimentally well-established pK_a of nicotinic acid as a reference.

$$\text{(1)}\quad \mathrm{UO_2C_5NH_5COO^{2+} + C_5NH_4COO^- \rightleftarrows UO_2C_5NH_4COO^+ + C_5NH_5COO}$$

3. Results and discussions

The geometry optimization of uranyl–nicotinate complexes, utilizing the cluster-continuum approach, confirmed the stable bidentate coordination of carboxylate to the uranyl equatorial plane (see Fig. 1). The inclusion of explicit water molecules adequately satisfied the remaining coordination sites, establishing a robust hydrogen-bonding network essential for accurate thermodynamic modeling. Using the isodesmic proton exchange reaction scheme, ΔG value was calculated to determine the pK_a of pyridine nitrogen in the uranyl-complexed state. By anchoring these calculations to the experimentally established pK_a of free nicotinic acid (4.80), the calculated pK_a for the uranyl-bound pyridine nitrogen was determined to be 1.43 at the ωB97X-D4 level of theory.

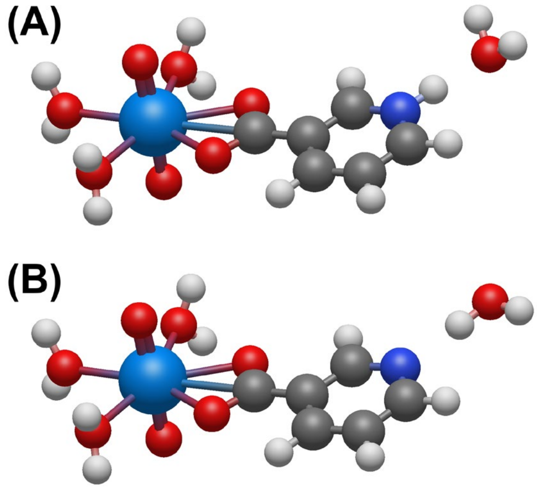

Fig. 1. Optimized structures of uranyl nicotinate complexes in aqueous solution: (A) $UO_2C_5NH_5COO^{2+}$ and (B) $UO_2C_5NH_4COO^{+}$.

These results demonstrate a significant structural and electronic consequence of complexation. Binding the highly charged uranyl moiety to the carboxyl group induces a pronounced electron-withdrawing effect across the heteroaromatic ring. This inductive withdrawal substantially decreases the electron density at the distal pyridine nitrogen, thereby facilitating deprotonation and lowering its pK_a by approximately 3.4 log units compared to the free ligand. The substantial acidification of nitrogen donor site carries important geochemical implications. Given the computed pK_a of 1.43, the pyridine group of uranyl-complexed ligand will exist exclusively in its deprotonated form across the typical pH ranges of natural waters. This fundamental shift in local charge distribution directly alters the overall net charge of complex structure. Understanding the precise chemical interaction between uranyl and model ligands serves as a fundamental building block for predicting the behavior of inherently complicated NOM. Our findings demonstrate that uranyl coordination exerts a strong inductive effect, significantly shifting the pK_a of nearby functional groups. Extrapolated to macromolecular NOM, such coordination can induce a cascade of deprotonation events, thereby altering the overall electrostatic charge and spatial conformation of molecular framework. Consequently, this state of deprotonation will strongly govern how uranyl-NOM complexes interact with background natural species and mineral components. Further, accurately evaluating such aqueous reaction parameters through DFT calculations provides a complementary approach to experimental methods for thermochemical database development. Ultimately, these findings enhance the predictive reliability of geochemical models for assessing the migration of uranium(VI) in diverse environmental systems.

4. Conclusion

This DFT study demonstrates that uranyl coordination fundamentally alters the molecular characteristics of nicotinic ligand. The strong electron-withdrawing effect of uranyl moiety induces a profound 3.4 log-unit acidification of the pyridine nitrogen (pK_a = 1.43). Consequently, this nitrogen-containing functional group remains fully deprotonated across typical environmental pH ranges. The critical shift in local charge distribution is expected to significantly dictates the electrostatic interactions and overall mobility of uranyl-organic complexes in diverse aqueous systems.

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