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A DFT Study on Thorium Complexation with Benzoic Acid in Aqueous Solution

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1. Introduction

Since thorium is redox-inactive and occurs exclusively as tetravalent species (Th^{4+} and its complexes) in aqueous media, it has been adopted as a chemical homologue of other tetravalent actinides—U(IV), Np(IV), and Pu(IV)—that predominate under the reducing conditions of deep geological repositories. Therefore, understanding the geochemical behavior of thorium is critical to assess the actinide migration within geological disposal systems, and thermodynamic data on Th(IV) serve as a reference for the An(IV) series [1]. Th(IV) speciation in natural waters is highly sensitive to the presence of natural organic matters (NOM), which contain a diverse functional groups capable of forming stable complexes with metal cations. Among these, aromatic carboxyl groups constitute a major binding motif of the natural macromolecules [2,3]. In particular, benzoic acid represents the simplest form of aromatic model ligands of NOM and has therefore been adopted to investigate the structural and thermochemical properties of actinide–NOM complexes [4–7]; its structure, a sole carboxyl group on a benzene ring, enables isolating the intrinsic Th(IV)–carboxylate interaction from the chelation and substituent effects inherent to more complicated molecules. Nevertheless, structural and thermodynamic elucidation of aqueous Th(IV)–benzoate complexation remain severely scarce, where only a single datum has been reported thus far [8]. Experimentally handling aqueous Th(IV)–organic ligand species is often challenging, particularly when it comes to separating the complexation from ubiquitously competing hydrolysis and to resolving specific binding modes that are not directly observable due to the low solubility of Th(IV). In this framework, density functional theory (DFT) is a powerful complementary approach that offers access to molecular electronic states and enables the prediction of Gibbs free energies, thereby facilitating the resolution of such ambiguities. Here, we employ the DFT method to elucidate the 1:1 and 1:2 Th(IV) benzoate complexes in all accessible binding modes, with the specific aim of quantifying the mode-dependent stabilities in an aqueous solution.

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 three hybrid functionals—B3LYP, PBE0, and ωB97X—each augmented with Grimme's D4 dispersion correction, to assess the functional dependence of computed thermodynamics. Scalar relativistic effects were treated with the zeroth-order regular approximation (ZORA). The all-electron relativistic SARC-ZORA-TZVP basis set was employed for thorium, while the ZORA-def2-TZVP basis set was used for light atoms (C, H, and O). The RIJCOSX approximation was applied, together with the corresponding auxiliary basis sets (SARC/J for thorium and def2/J for light atoms). To accurately simulate the aqueous environment, a cluster-continuum approach was adopted. Explicit water molecules were included to complete the nine-coordinate first hydration shell of Th(IV) in all species—$[Th(H_2O)_9]^{4+}$, the 1:1 benzoate complexes with bidentate (bi) or monodentate (mono) carboxylate binding, and the 1:2 complexes in the (bi,bi), (bi,mono), and (mono,mono) complexation modes—while free benzoate was represented as its monohydrate, and bulk solvation was accounted for using the SMD model.

3. Results and discussions

The geometry optimization calculations confirmed that both bi and mono bindings of benzoate to $[Th(H_2O)_9]^{4+}$ yield stable minima while the first hydration shell is retained. Notably, in the monodentate mode, a first-shell water donates an intramolecular hydrogen bond (1.58–1.67 Å) to the distal carbonyl oxygen of ligand, providing the compensation required for accurate thermodynamic calculations. Besides, to improve the accuracy of energetic calculations and to avoid uncertainties associated with direct calculation of solvation free energies of Th^{4+} cation, a disproportionation reaction scheme was employed. Specifically, the Gibbs free energy change (ΔG) of disproportionation of two 1:1 complexes into the free aqua Th^{4+} ion and a 1:2 complex was computed. Because the number of solute species is conserved between the reactants and products—so that standard state terms cancel out—the decrease in stepwise formation constants of 1:1 and 1:2 complexes ($\log K_1 - \log K_2 = \Delta G/(RT \ln 10)$) was directly obtained.

Using the disproportionation reaction scheme, ΔG values were calculated to determine the decrease in stepwise formation constants upon successive binding

of benzoate. The calculated ΔG was consistently positive, which was +8.4 to +8.7 kJ/mol at the ωB97X-D4 level of theory irrespective of the coordination mode combination. Such ΔG corresponds to log K_1 − log K_2 of ≈1.5, with all three functionals concurred on this quantity, with reaction energies agreeing to within ~3 kJ/mol. These results imply that successive complexation of benzoate to $[Th(H_2O)_9]^{4+}$ proceeds with only weak anti-cooperativity, not far above the statistical limit (~0.6 log units). This property is structurally rationalized as follows: complexation proceeds by substitution of first-shell waters at a conserved coordination number (=9), and each bound carboxylate lengthens the remaining Th–O bonds by merely 0.01–0.05 Å, indicating that the charge-accepting capacity of Th^{4+} center remains far from saturated even at the 1:2 stoichiometry.

Moreover, all binding-mode interconversions at fixed stoichiometry lie within ~6 kJ/mol of degeneracy, revealing a shallow coordination-mode range. The weak anti-cooperativity and mode flexibility provide important geochemical implications. Given the small decrease in stepwise formation constants, higher-order aqueous Th(IV)–carboxylate species remain readily accessible under ligand-rich conditions, and the near-degeneracy of binding modes implies that Th(IV) can accommodate geometrically constrained carboxylate sites with little energetic penalty. Understanding the precise chemical interaction between Th(IV) and model ligands serves as a fundamental building block for predicting the behavior of NOM. Extrapolated to NOM, such behavior enables progressive coordination of multiple carboxyl groups to An(IV), thereby neutralizing its effective charge and reshaping the hydration environment of resulting complexes. Ultimately, these findings enhance the predictive reliability of geochemical models for assessing the environmental migration of tetravalent actinides.

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