Key Words

actinide An(III)

lanthanides Ln(III)

phosphorus-oxygen-bonded ligands

solvent extraction

bipyridine phosphate ligand

electronic structure

desnsity functional theory (DFT)

selectivity

binding affinity

complexation

nuclear fuel cyclepartition and transmutation (P&T)

covalent interation

Gibbs free energy (G)

coodination chemistry

Objective

1. To investigate the extraction mechanisms of Am(III) and Eu(III) complexes with a bipyridine phosphate ligand using density functional theory (DFT) calculations.

2. To analyze the coordination modes of the complexes through bond length comparisons.

3. To determine the electronic structure, bonding properties, and thermodynamic behavior of Am(III) and Eu(III) complexes with bipyridine phosphate ligands.

4. To compare the bonding characteristics of the Am N and Eu N bonds and assess their covalent interactions.

5. To evaluate the selectivity of the bipyridine phosphate ligand for Am(III) over Eu(III) in terms of binding affinity.

6. To identify the most stable species during the complexation process using thermodynamic analysis.

7. To establish the potential of using the bipyridine phosphate ligand for effective separation of actinides (An(III)) and lanthanides (Ln(III)) in spent fuel reprocessing experiments.

8. To control the amount of nitrates in initial reactants and products to facilitate complex formation of Am3+ and Eu3+ with ligands.

9. To explore the implications of the study for the nuclear fuel cycle and the reprocessing of highly radioactive waste liquids.

10. To advance the understanding of factors that contribute to the extraction selectivity of phosphorus oxygen-bonded ligands

Methodology

1. Computational Chemistry Approach: Due to the high experimental costs associated with studying highly radioactive actinides, a computational chemistry approach was adopted.

2. Software and Methodology:

- The calculations were performed using Gaussian 09 software.

- The B3LYP method in density functional theory (DFT) was employed. This method combines features of the Hartree-Fock method with DFT, using the exchange functional of Becke 88 and the three-parameter functional (B3) with the correlation functional developed by Lee, Yang, and Parr (LYP)

3. Modeling Actinides and Lanthanides:

- Am(III) and Eu(III) were chosen to represent actinides and lanthanides, respectively.

- Small core pseudopotentials (quanti-relativistic effective core potentials, RECP) were used to replace 60 inner core electrons in Am and 28 inner core electrons in Eu. The remaining electrons were treated as valence electrons

4. Basis Sets:

- For light elements such as C, H, O, and N, 6-31G(d) or 6-311G(2df,p) basis sets were utilized.

- Vibrational frequencies of optimized stable systems at the B3LYP/6-31G(d)/RECP level of theory were analyzed to ensure real frequencies represented local minima in terms of energy on the potential energy surface

5. Quantum Theory of Atoms in Molecules (QTAIM) Analysis: Multiwfn 3.8 software was used to conduct QTAIM analysis to investigate the bond characteristics between metal ions and ligands at the same level of theory

6. Natural Bond Orbital (NBO) Analysis: NBO analysis was performed to elucidate the electronic and bonding characteristics of water-soluble ligands containing phosphorus oxygen bonds with Am(III) and Eu(III) at the B3LYP//ECP60MWB-SEG/6-311G* level

7. Solvation Effects: Single-point energy computations were executed in various solvent environments (aqueous, cyclohexanone, and nitrobenzene solutions) to accurately model the environment and account for solvation effects using the solvation model-based density (SMD)

8. Optimization of Complexes:

- Four separate complexes of Am(III) and Eu(III) with bipyridine phosphate ligands were optimized, each containing different quantities of nitrate anions and water molecules.

- The optimized structures of the 1:1 species $AmL(NO_3)_3$/$EuL(NO_3)_3$ and the 1:2 species $[AmL_2NO_3]_{2+}$/$[EuL_2NO_3]_{2+}$ were analyzed. All nitrate anions coordinated in a bidentate manner with the metal ions

Key Findings

3.1 Bipyridyl Phosphate Ligands:

Chemical Reactivity: The electrostatic potential (ESP) analysis indicated that the N and O1 atoms are rich in electrons, facilitating their coordination with metal ions.

Electronic Structure: The energy gap between HOMO and LUMO provided insight into the molecules reactivity, indicating that the N and O1 atoms are likely reaction sites.

Symmetry: The optimized ligand structure exhibited approximate C2 symmetry

3.2 Study of Am(III) and Eu(III) Complexes with Bipyridyl Phosphate Ligands

Hydrated Species: The central metal ions had coordination numbers of 9, with nitrate anions coordinating in a bidentate manner.

Optimized Complexes: Four different complexes of Am(III) and Eu(III) with bipyridine phosphate ligands were optimized. All nitrate anions coordinated in a bidentate manner with the metal ions

3.3 Bonding Nature:

Wiberg Bond Index (WBI): The Am NL bond exhibited a higher average WBI compared to the Eu NL bond, implying a stronger bonding interaction between the nitrogen donor and Am(III) ions.

Mayer Bond Order (MBO): MBO values confirmed that the Am N bond had more pronounced covalent properties than the Eu N bond.

Quantum Theory of Atoms in Molecules (QTAIM): QTAIM analysis indicated that M OL bonds were stronger than M NL bonds, primarily because oxygen had a higher electronegativity than nitrogen

3.4 Energy Analysis

Gibbs Free Energy (G): The G values for various complexation reactions were calculated, indicating that reactions involving Am(III) complexes were more thermodynamically favorable than

those involving Eu(III) complexes.

Theromodynamic Favorability: The 1:1 extraction reaction was more effective for the separation of Am(III) and Eu(III), with optimal separation achievable through the modulation of experimental conditions.

Solvation Effects: Reactions in aqueous, cyclohexanone, and nitrobenzene solutions showed different thermodynamic favorabilities, with aqueous solutions being less favorable for separation processes compared to organic solvents

Relevance to Study

Effective Separation: The study demonstrates that bipyridyl phosphate ligands show strong potential for effectively separating actinides (An(III)) from lanthanides (Ln(III)), a critical step in nuclear fuel reprocessing

Selective Extaction: The bipyridyl phosphate ligand exhibits higher selectivity for Am(III) over Eu(III), attributed to the stronger covalent interaction between the ligand and Am(III) ions

Thermodynamic Favorability: Thermodynamic analyses indicate that the complexation of Am(III) with the ligand is more favorable than that of Eu(III), supporting its use in selective extraction processes

Coordination Chemistry: The study provides detailed insights into the coordination modes and bonding nature of the ligands with metal ions, emphasizing the role of nitrogen and oxygen atoms in the ligand structure

Computational Validation: The use of density functional theory (DFT) and other computational methods validates the ligand's performance, reducing the need for extensive experimental testing

Potential for Spent Fuel Reprocessing: The findings suggest that bipyridyl phosphate ligands can be integrated into spent fuel reprocessing workflows to improve the separation efficiency of minor

actinides from lanthanides, supporting the goals of partition and transmutation strategies

Environmental Impact: By facilitating the separation of minor actinides, the use of these ligands can contribute to reducing the volume and toxicity of high-level nuclear waste, thereby mitigating environmental hazards

Scalability: The study highlights the potential for scaling up the use of bipyridyl phosphate ligands in industrial applications, addressing the practical aspects of ligand design and implementation in nuclear fuel cycles

Novel Ligand Design: The research paves the way for designing new derivatives of bipyridyl phosphate ligands with enhanced selectivity and stability, crucial for advancing nuclear fuel reprocessing technologies

Support for Experimental Studies: Theoretical insights from this study can guide future experimental efforts, focusing on optimizing ligand structures and extraction conditions to achieve better separation performance

Critical Parameters Identified

High Importance

Chemical Stability: The bipyridyl phosphate ligand's stability was not explicitly discussed in terms of hydrolysis or reactivity with other chemicals. However, the study's computational focus implies an assumption of chemical stability under the conditions modeled

Radiolysis Resistance: The study did not explicitly address radiolysis resistance. This is an area that would need experimental validation to ensure the ligand's stability under radioactive conditions.

Thermodynamics: Extensive thermodynamic analysis was conducted, indicating that the reactions involving Am(III) complexes were more thermodynamically favorable than those involving Eu(III) complexes. This demonstrates the ligand s potential for selective extraction of Am(III) over Eu(III)

Medium Importance

Kinestics (forwards and reverse): The study did not directly address the kinetics of the ligand's interactions with metal ions. This is a gap that would require further experimental or computational investigation.

Loading Capacity: The study did not provide specific details on the loading capacity of the ligand. The focus was more on the selectivity and thermodynamic favorability of the complexes formed

Operational Condition Range: The ligand s ability to function under various solvent environments (aqueous, cyclohexanone, nitrobenzene) was discussed, indicating flexibility in operational conditions

Low Importance

Solubility: Solubility issues were implied through the discussion of different solvent environments used in the study. The bipyridyl phosphate ligand s compatibility with these solvents suggests manageable solubility

Dispersion Numbers: The study did not address dispersion numbers. This factor would be more relevant in applied system evaluations rather than in theoretical studies.

Phase Disengagement: Phase disengagement was not discussed. The focus was on the molecular interactions and thermodynamics rather than the practical separation of phases post-extraction