

Key Words

uranium (VI)

thorium (IV)

selective complexation

separation

Tetradentate N,O-Hybrid Ligands

Et-Tol-BPDA (N,N -diethyl-N,N -di-p-tolyl-2,2 -bipyridine-6,6 -dicarboxamide)

Et-Tol-BPymDA (N,N -diethyl-N,N -di-p-tolyl-2,2 -bipyrimidine-4,4 -dicarboxamide)

synthesis

extraction

spectroscopy

Objective

1. Design and Synthesis of New Ligands: Synthesize two new tetradentate N,O-hybrid ligands, specifically N,N -diethyl-N,N -di-p-tolyl-2,2 -bipyridine-6,6 -dicarboxamide (Et-Tol-BPDA) and N,N -diethyl-N,N -di-p-tolyl-2,2 -bipyrimidine-4,4 -dicarboxamide (Et-Tol-BPymDA).
2. Evaluate Extraction Performance: Assess the extraction abilities and selectivities of these ligands for U(VI) over Th(IV) under various conditions, including different concentrations of nitric acid and ligand.
3. Understand Extraction Mechanism: Investigate the extraction mechanisms of these ligands by conducting solvent extraction experiments and analyzing the thermodynamics and stoichiometry of the extracted complexes.
4. Characterize Ligand-Metal Complexes: Characterize the formed complexes using techniques such as UV-Vis spectroscopy, slope analysis, and single-crystal X-ray diffraction to determine the

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coordination modes and stability of the complexes.

5. Thermodynamic Studies: Conduct thermodynamic studies to understand the spontaneity and driving forces behind the extraction processes for U(VI) and Th(IV) using these ligands.

Methodology

1. Chemical Reagents and Equipment:

- Utilized various chemical reagents including 2,2'-bipyridine-4,4'-dicarboxylic acid, 2-chloro-4-methylpyrimidine, and N-ethyl-p-toluidine.
- Employed equipment such as ^1H NMR and ^{13}C NMR spectrometers, and a high-resolution liquid chromatograph coupled with a mass spectrometer.

2. Synthesis of Ligands:

- Synthesized two ligands: N,N'-diethyl-N,N'-di-p-tolyl-2,2'-bipyridine-6,6'-dicarboxamide (Et-Tol-BPDA) and N,N'-diethyl-N,N'-di-p-tolyl-2,2'-bipyrimidine-4,4'-dicarboxamide (Et-Tol-BPymDA).
- Specific synthesis procedures involved refluxing and purification steps, described in the supporting information.

3. Solvent Extraction Experiments:

- Conducted experiments with U(VI) and Th(IV) in various nitric acid concentrations.
- Prepared the organic phase by dissolving ligands in C4mimNTf2 or other organic diluents.
- Mixed equal volumes of the organic and aqueous phases, shook for 6 hours, and analyzed the aqueous phase using ICP-OES.

4. UV-Vis Spectroscopic Titration:

- Carried out spectroscopic experiments in acetonitrile at 298 K.
- Titrated ligand solutions with $\text{UO}_2(\text{NO}_3)_2$ or $\text{Th}(\text{NO}_3)_4$, fixed ionic strength with

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tetraethylammonium nitrate, and collected absorption spectra .

5. Preparation of Single-Crystal Complexes:

- Prepared single-crystal complexes of the synthesized ligands with U(VI) and Th(IV).
- Employed slow evaporation methods and characterized the structures using single-crystal X-ray diffraction .

6. Thermodynamic Studies:

- Implemented solvent extraction experiments at temperatures ranging from 293.15 to 313.15 K.
- Calculated thermodynamic parameters, including enthalpy change, entropy change, and Gibbs free energy change, to understand the extraction behavior

7. Stripping Studies:

- Examined the back extraction (stripping) of U(VI) from the loaded organic phase.
- Tested various stripping agents and determined the metal ion concentration in the aqueous phase after extraction .

8. Extraction Mechanism Elucidation:

- Investigated the extraction mechanism by testing variations in the distribution ratio of U(VI) and Th(IV) as a function of C4mim⁺ or NTf₂⁻ concentration.
- Concluded that the extraction mechanism follows the solvation mechanism based on the co-extraction of nitrate anions .

9. Influence of Nitric Acid Concentration:

- Studied the effect of varying nitric acid concentrations on the extraction efficiency.
- Found that extraction percentages were negligible below 4 M HNO₃ but increased at higher acidities .

10. Complexation Behavior and Coordination Mode:

- Performed UV-Vis spectroscopic experiments and Job plot analyses to determine the stoichiometry

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and coordination mode of the complexes formed.

- Analyzed the data to rationalize the selectivity of the ligands for U(VI) over Th(IV) .

Key Findings

1. Synthesis and Characterization:

- The ligands Et-Tol-BPDA and Et-Tol-BPymDA were successfully synthesized.
- The crystal structures of these ligands were determined using single-crystal X-ray diffraction.
- Both ligands exhibited a planar conformation with specific torsion angles that stabilized their structures.

2. Extraction Performance

- The extraction efficiencies of U(VI) and Th(IV) were evaluated.
- It was found that Et-Tol-BPDA exhibited higher extraction efficiency compared to Et-Tol-BPymDA.
- The difference in extraction efficiencies was attributed to the electron-withdrawing effects of the additional nitrogen atoms in Et-Tol-BPymDA, leading to lower natural charges near the amide groups.

3. Influence of Ligand Concentration

- The extraction efficiencies increased with increasing ligand concentration, indicating the formation of 1:1 complexes between ligands and metal ions.
- Slope analysis confirmed the 1:1 complexation during the extraction process.

4. Stripping Study

- The study examined the back extraction of U(VI) from the loaded organic phase.
- Deionized water and 0.01 M HNO₃ effectively stripped U(VI) from the Et-Tol-BPymDA/C4mimNTf₂ system, while a solution of 0.05 M EDTA-2Na and 1 M guanidine carbonate was needed for the Et-Tol-BPDA/C4mimNTf₂ system.

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5. Extraction Mechanism Elucidation:

- The extraction mechanism involved the solvation mechanism, with variations in the distribution ratio of U(VI) and Th(IV) as functions of ligand and ionic liquid concentrations.
- The extraction was found to be driven by complexation between the ligands and metal ions.

6. Thermodynamic Studies:

- The extraction processes were evaluated at different temperatures.
- For Et-Tol-BPDA, the extraction was endothermic, while for Et-Tol-BPymDA, it was exothermic.
- Thermodynamic parameters indicated that the extraction of U(VI) was more favorable than that of Th(IV).

7. UV-Vis Titration Analysis:

- UV-Vis spectroscopic experiments confirmed the 1:1 stoichiometry between ligands and metal ions.
- The stability constants obtained from UV-Vis titration experiments demonstrated higher binding affinities of Et-Tol-BPDA and Et-Tol-BPymDA towards uranyl ions compared to thorium ions.

8. Single Crystal Complexes:

- Single-crystal complexes of the ligands with U(VI) and Th(IV) were prepared and characterized.
- The uranyl ion was bonded to the ligands in a near-planar conformation, while the thorium ion formed spherical complexes with the participation of nitrate anions.

9. Influence of Contact Time

- The extraction kinetics for both U(VI) and Th(IV) showed that equilibrium was reached at 120 minutes for Et-Tol-BPDA and 180 minutes for Et-Tol-BPymDA.

10. Distribution Ratios:

- The distribution ratios of U(VI) and Th(IV) increased with the concentration of nitric acid, ligand, and ionic liquids, indicating the complexation as the driving force for extraction.

Conclusion

- Two new tetradentate N,O-hybrid ligands, Et-Tol-BPDA and Et-Tol-BPymDA, were synthesized for the selective complexation and extraction of U(VI) over Th(IV) in highly acidic conditions.
- The study achieved high separation factors (SFU/Th) for both ligands, demonstrating their potential for uranium extraction in the thorium-uranium fuel cycle.
- Thermodynamic and kinetic analyses, along with spectroscopic and crystallographic characterizations, provided insights into the mechanisms driving the selective extraction of U(VI) over Th(IV).

Relevance to Study

Design and Synthesis: Developed two new tetradentate N,O-hybrid ligands, Et-Tol-BPDA and Et-Tol-BPymDA, which are significant for selective uranium extraction from thorium, addressing challenges in the thorium-uranium fuel cycle

Extraction Efficiency: Demonstrated high extraction efficiencies and selectivity for U(VI) over Th(IV), essential for effective uranium recovery from spent nuclear fuel

Mechanism Elucidation: Identified the solvation mechanism as the primary extraction process, providing insights into the interaction between ligands and metal ions, which is crucial for designing efficient extractants

Thermodynamic and Kinetic Studies: Conducted comprehensive thermodynamic and kinetic studies, showing that the extraction processes are spontaneous and identifying optimal conditions for efficient extraction, which helps in the practical application of these ligands in nuclear fuel reprocessing

Spectroscopic and Crystallographic Characterization: Used UV-Vis spectroscopy and single-crystal

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X-ray diffraction to characterize the ligand-metal complexes, revealing their structural properties and binding affinities, crucial for understanding the coordination chemistry involved

High Acidity Conditions: Demonstrated the ligands' effectiveness in highly acidic environments (up to 3 M HNO₃), relevant for real-world nuclear fuel reprocessing conditions where high acidity is often present

Ligand Stability: Proved the stability of the ligands in strong acidic solutions, an essential factor for their durability and effectiveness in long-term nuclear fuel reprocessing applications

Potential Applications: Highlighted the potential of bipyridine- and bipyrimidine-derived diamide ligands for uranium/thorium separation, paving the way for their use in advanced nuclear fuel cycles and enhancing the sustainability of nuclear energy

Comparative Analysis: Provided a comparative analysis with existing ligands, showing superior performance in uranium extraction, which informs future ligand design and selection

Environmental Impact: By improving the efficiency of uranium extraction from thorium, the study contributes to reducing the environmental impact of nuclear waste, aligning with the goals of green chemistry and sustainable nuclear energy

Critical Parameters Identified

High Importance

Chemical Stability: The ligands Et-Tol-BPDA and Et-Tol-BPymDA were synthesized and characterized, showing stability in strong acidic solutions up to 3 M HNO₃, which is crucial for their durability and effectiveness in nuclear fuel reprocessing

Radiolysis Resistance: Although the study does not directly address radiolysis resistance, the stability of the ligands in highly acidic conditions suggests potential resilience under radiolytic conditions common in nuclear environments

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Thermodynamics: Comprehensive thermodynamic studies revealed that the extraction processes are spontaneous at room temperature, with specific enthalpy and entropy changes indicating favorable conditions for the selective extraction of U(VI) over Th(IV). The thermodynamic parameters highlight the feasibility and efficiency of the ligands for nuclear fuel cycle applications

Medium Importance

Kinetics: The extraction kinetics for U(VI) and Th(IV) were investigated, showing that equilibrium was reached at 120 minutes for Et-Tol-BPDA and 180 minutes for Et-Tol-BPymDA. Efficient kinetics ensure that the separation process occurs within practical time frames

Loading Capacity: The study examined the ligand concentration's impact on extraction efficiency, indicating that higher ligand concentrations improved the extraction performance, thereby demonstrating the ligands' capacity to process substantial amounts of material before saturation

Operational Condition Range: The ligands were tested under various conditions, including different nitric acid concentrations and temperatures, showcasing their ability to operate effectively across a broad range of conditions, which enhances their flexibility and applicability in nuclear fuel reprocessing

Low Importance

Solubility: The solubility of the ligands in different solvents, including ionic liquids, was evaluated. Both ligands showed good solubility in the selected solvents, which is important but manageable compared to other factors

Dispersion Numbers: The study does not explicitly discuss dispersion numbers, but the effective mixing and phase separation achieved during the extraction experiments imply efficient mass transfer between phases

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Phase Disengagement: Phase disengagement was managed effectively during the extraction and stripping studies, ensuring practical separation of the organic and aqueous phases after extraction. This aspect, while critical for applied systems, was successfully handled under the study's conditions