

Key Words

lanthanide ocomplexes

actinide/lanthanide separation

Bis-1,2,3-triazole-bipyridine Ligands (BTzBPs)

complexation

solvent extraction

Objective

1. Investigation of Lanthanide Complexation:

- The article aims to investigate the complexation of selected trivalent lanthanide ions with derivatives of tetranitrogen donor ligands, specifically 6,6'-bis-1R,1H-1,2,3-triazol-4-yl-2,2'-bipyridines (BTzBPs).

2. Synthesis and Characterization of Complexes:

- The synthesis and characterization of an anhydrous solid lanthanide complex, [Ce(Bn-BTzBP)(NO₃)₃], using single-crystal X-ray diffraction.

3. Spectroscopic Studies:

- The use of time-resolved fluorescence spectroscopy to study Eu(III) complexes with BTzBP ligands in solution and to investigate the influence of 2-bromohexanoic acid on Eu(III) complexes.

4. Understanding Extraction Process

- To help identify the species formed during the extraction process and to understand the role of 2-bromohexanoic acid in the separation system.

5. Comparison with Other Lanthanides:

- The comparison of stability constants of Eu(III) with other lanthanide complexes using UV-visible spectrophotometry to gain insight into their complexation behavior.

Methodology

1. Synthesis of Complexes:

Synthesis of Ce(III) Bn-BTzBP Nitrate Crystals: Bn-BTzBP was dissolved in dichloromethane, and a solution of cerium(III) nitrate in ethanol was layered on top. After three days of slow diffusion, yellow plate-like crystals were obtained suitable for single-crystal X-ray diffraction studies.

2. Characterization Techniques:

Single-Crystal X-ray Diffraction: Crystallographic studies were conducted to determine the structure of the synthesized Ce(Bn-BTzBP)(NO₃)₃ complex. Intensity measurements were performed using a Bruker Quest diffractometer with Mo K α radiation, and the structure was solved using standard software and refined by full-matrix least-squares techniques.

UV-Vis-NIR Spectroscopy: UV-visible-near-infrared absorption data were acquired from a single crystal of Ce(Bn-BTzBP)(NO₃)₃ to support the oxidation state assignment.

Time-Resolved Fluorescence Spectrometry (TRFS): Europium complexes in methanol were studied by TRFS. Emission spectra and fluorescence lifetimes were measured to characterize the Eu(III) complexes and understand the influence of 2-bromohexanoic acid.

3. Solution Studies:

Fluorescence Titrations: Titrations of Eu-containing solutions with EH-BTzBP were performed in methanol (with 1% water) to identify metal/ligand complexes. Changes in fluorescence spectra were monitored to model the speciation and determine stability constants using Hypspec software.

UV-Visible Spectrophotometry: Spectrophotometric titrations were performed to compare the stability constants of Eu(III) with other lanthanide complexes. EH-BTzBP was titrated with Ln(NO₃)₃ solutions in methanol, and absorbance changes were recorded and analyzed.

4. Influence of 2-Bromohexanoic Acid:

- The impact of 2-bromohexanoic acid on Eu(III) complexes was investigated by adding the acid to

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methanol solutions and observing changes in fluorescence spectra and lifetimes.

5. Comparative Studies in Different Media:

- Comparisons were made between the fluorescence properties of Eu(III) in nitrate and perchlorate media to understand the presence and role of counterions in the first coordination sphere of Eu(III) complexes.

6. Titration in Organic Solvents:

- Titration experiments were repeated in toluene to determine the effect of the diluent on coordination. Eu(III) was extracted into toluene, and the evolution of the Eu(III) fluorescence spectrum was monitored upon addition of EH-BTzBP and 2-bromohexanoic acid.

Key Findings

X-ray Crystallography

1. Structure Determination

- The Ce(III) complex with Bn-BTzBP ($\text{Ce}(\text{Bn-BTzBP})(\text{NO}_3)_3$) was characterized by single-crystal X-ray diffraction.
- The structure revealed a Ce(III) ion coordinated to one tetradentate Bn-BTzBP ligand and three chelating bidentate nitrate ions, forming a 10-coordinate environment around the metal center.
- The Ce O and Ce N bond distances were indicative of Ce(III), confirming no oxidation to Ce(IV).

2. Comparison with Similar Complexes

- The Ce O bond distances were similar to those found in other lanthanide BTBP complexes.
- The Ce N bond distances in the Bn-BTzBP complex were shorter than those in the corresponding BTBP complexes, indicating a tighter coordination.

Spectrofluorimetry

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1. Europium Complexes in Nitrate Medium:

- The study revealed the formation of 1:1 and 1:2 Eu(III)-EH-BTzBP complexes in methanol.
- The fluorescence lifetimes and emission spectra indicated a complete dehydration of the 1:1 complex, suggesting full coordination by the tetradentate ligand and inner-sphere nitrate ions.
- The 1:2 complex was also fully dehydrated, implying the presence of two tetradentate ligands in the inner coordination sphere

2. Effect of Perchlorate Medium:

- In the perchlorate medium, different spectral properties and shorter fluorescence lifetimes were observed, indicating the presence of perchlorate ions in the outer coordination sphere.
- The 1:1 Eu(III)-EH-BTzBP complex in the perchlorate medium had a lower fluorescence lifetime compared to the nitrate medium, suggesting methanol molecules filled the remaining coordination sites.

3. Presence of 2-Bromohexanoic Acid (HA):

- Minimal changes in the fluorescence spectra and lifetimes indicated that HA did not significantly replace nitrate ions in the inner sphere in methanol.
- The presence of HA in the perchlorate medium resulted in spectra similar to those found in literature, confirming its presence in the inner sphere of Eu(III) in methanol.

Titration in Toluene

1. Europium Extraction:

- The Eu(III) complexes formed in toluene were similar to those in methanol, indicating the formation of 1:1 and 1:2 complexes.
- Fluorescence lifetimes suggested the formation of Eu-HA complexes initially, which were replaced by EH-BTzBP ligands during titration.

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2. Coordination Environment

- The presence of three HA molecules or dimers in the outer coordination sphere to achieve electroneutrality of the complex was indicated.

Ultraviolet Absorption Spectrophotometry

1. Lanthanide Complexation:

- UV absorption spectra confirmed the formation of 1:1 and 1:2 complexes of EH-BTzBP with Nd(III), Eu(III), and Ho(III) in methanol.
- Stability constants obtained from UV spectrophotometry were consistent with those from spectrofluorimetry, demonstrating reliable complexation behavior.

2. Comparison with BTBP Ligands:

- The stability constants for EH-BTzBP complexes were lower than those for BTBP ligands, explaining the lower extraction efficiency observed for EH-BTzBP.

Conclusion

1. Overall Findings

- The study demonstrated that the EH-BTzBP ligand forms stable 1:1 and 1:2 complexes with lanthanides in both solid and solution states.
- The role of 2-bromohexanoic acid as a co-extractant was elucidated, with findings indicating its importance in the phase transfer process.
- The results provided insights into the coordination environment and stability of the lanthanide complexes, contributing to the understanding of actinide/lanthanide separation processes.

Relevance to Study

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Stability Under Radiolytic Conditions:

- EH-BTzBP ligands exhibited no signs of degradation under highly acidic and oxidative conditions, crucial for maintaining functionality in the nuclear fuel cycle.

Selective Extraction:

- The study demonstrated high selectivity of EH-BTzBP for americium over lanthanides, which is essential for efficient separation in nuclear reprocessing.

Coordination Environment:

- Detailed analysis of coordination complexes provided insights into the binding interactions and structural stability of ligands with lanthanides, aiding in the selection of robust ligands.

Phase Transfer Kinetics:

- EH-BTzBP showed rapid phase-transfer kinetics, which is beneficial for practical application in solvent extraction processes.

Effect of Co-extractants:

- The role of 2-bromohexanoic acid as a co-extractant was identified, highlighting the importance of combining ligands with co-extractants to improve extraction efficiency.

Comparative Analysis:

- Stability constants and complexation behavior of EH-BTzBP were compared with BTBP ligands, providing a basis for selecting ligands with superior performance.

Critical Parameters Identified

High Importance

1. Chemical Stability: EH-BTzBP ligands showed no signs of degradation under highly acidic and oxidative conditions, indicating excellent chemical stability.
2. Radiolysis Resistance: The study did not explicitly address radiolysis resistance. However, the

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stability under oxidative conditions suggests potential resilience to radiolytic degradation.

3. Thermodynamics: Stability constants for the 1:1 and 1:2 Eu(III) complexes with EH-BTzBP were determined ($\log K_1 = 4.8$, $\log K_2 = 9.2$), indicating the feasibility and selectivity of the separation process at a fundamental thermodynamic level.

Medium Importance

1. Kinetics: The study reported rapid phase-transfer kinetics for EH-BTzBP, which is beneficial for practical application in solvent extraction processes, ensuring efficient and timely separation.
2. Loading Capacity: The document did not explicitly address the loading capacity of the ligands.
3. Operational Condition Range: EH-BTzBP ligands were stable and effective under a range of conditions, including highly acidic environments, enhancing their applicability in diverse operational settings.

Low Importance

1. Solubility: Solubility issues were noted for the Bn-BTzBP ligand in suitable diluents, leading to the use of EH-BTzBP instead, which was more soluble and suitable for the studies.
2. Dispersion Numbers: The study did not address dispersion numbers.
3. Phase Disengagement: Phase disengagement was not specifically discussed, but the effective phase-transfer kinetics implies good phase separation characteristics in the extraction process.