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Key Words

europium (III)

diglycolamide

coordination chemistry

solvent extraction

Extended X-ray Absorption Fine Structure (EXAFS)

Objective

1. Synthesize and characterize the homoleptic, cationic europium(III) complex with three neutral tetraalkyldiglycolamide ligands.
2. Examine the inner-sphere coordination of the Eu3+ ion using Eu L3-edge X-ray absorption spectroscopy (XAS).
3. Propose a structural model for the coordination environment of Eu3+ in the complex.
4. Understand the impact of ligand structure and counterion presence on the coordination and extraction efficiency.
5. Lay the foundation for advanced solvent extraction processes for separating minor, tripositive actinides (Am, Cm) from lanthanide ions based on the local structure of Eu3+ in the solid-state coordination complex with TODGA.

Methodology

Synthesis

1. Materials:

Europium chloride hexahydrate (99.9%)

Anhydrous bismuth chloride (99.9%)

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N,N,N ,N -Tetraoctyldiglycolamide (TODGA)

Methanol (Reagent ACS/USP/BP grade)

Trace metal grade hydrochloric acid (37%)

Nitric acid (70%)

Silver nitrate (99+%)

Hydrogen peroxide (30%)

ASTM reagent grade II deionized water

2. Procedure:

- Dissolve 1.00 gram of anhydrous bismuth chloride, 0.37 gram of europium chloride hexahydrate, 1.0 mL of 37% hydrochloric acid, and 1.86 grams of TODGA in 100 mL of methanol.
- Filter the solution using a 24 mm, 0.45 m pore size polyethersulfone syringe filter to remove residual solids (likely BiOCl).
- Add deionized water dropwise while stirring until a white precipitate forms.
- Continue stirring for one hour.
- Isolate the solid by vacuum filtration on Whatman no. 42 ashless filter paper and wash with three portions of 5 mL 50% (v/v) methanol in deionized water.
- Transfer the white precipitate to a 20 mL borosilicate glass vial and dry in an oven at 70 C for 24 hours

Metal Analyses

1. Europium and Bismuth Content:

- Weigh 1.01 grams of the dried metal-TODGA complex into a zirconium crucible.
- Fire the sample in a muffle oven at 800 F for 8 hours to destroy the organic portion.
- Dissolve the residual white solid in 10 mL of 70% HNO3 and 500 L of 30% H2O2, transfer to a

250 mL glass volumetric flask, and dilute to 250 mL with deionized water.

- Analyze europium (381.967 nm) and bismuth (306.772 nm) contents using an Agilent Technologies 4100 microwave plasma atomic emission spectrometer (MP-AES)

Chlorine Analysis

1. Procedure:

- Dissolve 0.50 gram of the dried metal-TODGA complex in 40 mL of anhydrous methanol by heating in a water bath at 40 C.
- Add silver nitrate (0.60 g in 40 mL of methanol) slowly while stirring to form a white precipitate (AgCl).
- Continue stirring for 2 hours to ensure complete exchange and precipitation of the Cl as AgCl.
- Transfer the precipitate and supernate to two 50 mL polypropylene centrifuge tubes and centrifuge at 2000 rpm for 10 minutes.
- Wash the precipitate with 2   10 mL of methanol and then 2   10 mL of 1 M HNO3.
- Transfer the washed precipitate to a tared zirconium crucible and dry at 130 C until a constant weight is achieved.
- Dissolve the AgCl precipitate in NH4OH (NH4)2NO3 followed by 70% HNO3.
- Analyze the dissolved precipitate by MP-AES to identify Ag content and verify Bi and Eu contents below detection limits

X-ray Absorption Fine Structure (XAFS) Analysis

1. Procedure

- Acquire Europium L3-edge X-ray absorption spectra for a pressed pellet of Eu(TODGA)3(BiCl4)3 at room temperature using a multi-element fluorescence detector at beamline 12-BM-B of the

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Advanced Photon Source at Argonne National Laboratory.

- Perform all analyses with EXAFSPAK, curve fitting the k3 (k) EXAFS with phase and amplitude functions from FEFF8.0 and a fixed scale factor using models of Eu^{3+} coordination with O and C atom neighbors

Key Findings

1. Eu^{3+} Coordination Environment: The study revealed that the Eu^{3+} ion in the $[Eu(TODGA)_3][(BiCl_4)_3]$ complex is coordinated by nine oxygen atoms from three TODGA ligands in a tridentate fashion, forming six five-membered chelate rings. The coordination includes two carbonyl oxygen atoms and one ether oxygen atom from each TODGA ligand.
2. EXAFS Analysis: Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy showed distinct peaks corresponding to the coordination of Eu^{3+} with carbon atoms (both sp2-hybridized carbonyl carbons and sp3-hybridized ether carbons), confirming the tridentate coordination model.
3. Structural Stability: The n-octyl groups on TODGA ligands do not perturb the Eu^{3+} coordination environment significantly, indicating that the structural rigidity of the tridentate coordination is maintained despite the length and flexibility of the alkyl chains.
4. Implications for Solvent Extraction: The findings provide a structural basis for understanding the performance of TODGA in solvent extraction processes, particularly in separating minor actinides (Am, Cm) from lanthanides. The study suggests that the coordination chemistry plays a crucial role in the extraction efficiency and speciation of the complexes in solution.
5. Future Applications: The results set the foundation for further research on advanced solvent extraction processes, such as the ALSEP process, by providing insights into the coordination environment and stability of Eu^{3+} complexes with TODGA, which can be applied to improve the separation of lanthanides and actinides in nuclear fuel reprocessing

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Relevance to Study

Coordination Environment Insight: The study provides detailed structural information on the coordination of Eu(III) with diglycolamide ligands, essential for selecting ligands that efficiently bind to lanthanides and actinides during solvent extraction

Thermodynamics and Structural Stability: Understanding the stability and rigidity of the Eu(TODGA)3 complex contributes to selecting ligands that maintain their structural integrity under the harsh conditions of nuclear fuel reprocessing

Radiation Resistance: he structural insights provided by the EXAFS analysis suggest that the Eu(III) complex's coordination environment is resilient, which is crucial for ligands to withstand radiolytic conditions in nuclear applications

Separation Efficiency: The findings indicate how the TODGA ligand can be used to separate minor actinides (Am, Cm) from lanthanides, addressing one of the significant challenges in nuclear waste management

Foundation for Advanced Processes: The structural model and coordination chemistry insights form a basis for developing advanced solvent extraction processes like ALSEP, optimizing ligand selection for efficient and selective extraction of specific ions in the nuclear fuel cycle

Critical Parameters Identified

Hgih Importance

1. Chemical Stability: The study shows that the tridentate coordination motif of TODGA with Eu(III) remains stable even with the presence of large n-octyl groups, indicating good chemical stability under the conditions tested

2. Radiolysis Resistance: While the article does not directly address radiolysis resistance, the structural stability of the Eu(TODGA)3 complex suggests potential resilience to radiolytic conditions,

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an important factor for ligands in nuclear applications

3. Thermodynamics: The EXAFS analysis provides thermodynamic data on the coordination of Eu(III) with TODGA, highlighting the feasibility of forming stable complexes, which is essential for efficient separation processes

Medium Importance

1. Kinetics: The study provides insights into the structure of the Eu(III) complex but does not explicitly cover the kinetics of the separation process. However, understanding the structural stability indirectly supports efficient kinetic behavior
2. Loading Capacity: The structural data suggests that TODGA can form stable complexes with Eu(III), implying a potentially high loading capacity for lanthanides and actinides in separation processes
3. Operational Condition Range: The study demonstrates that the TODGA ligand forms stable complexes under the conditions tested, indicating its applicability across a range of conditions likely encountered in nuclear fuel reprocessing

Low Importance

1. Solubility: The solubility of the complex in methanol and the use of different solvents for washing and analysis suggest that solubility can be managed through solvent selection
2. Dispersion Numbers: The study does not specifically address dispersion numbers, as the focus is more on the structural and coordination aspects of the complex
3. Phase Disengagement: Phase disengagement is not explicitly covered in the study, but the stable coordination complex formation implies effective separation, which is indirectly related to phase disengagement efficiency