

Key Words

lanthanide

cyclopentadienyl

complexes

EPR

spectroscopy

hyperfine

relaxation

crystallography

covalency

ligand

electron

bonding

paramagnetic

magnetic

spin

Objective

1. To investigate trends in metal arene interactions across a series of early lanthanide (Ln) complexes $[\text{Ln}(\text{Cptt})_3]$ (Ln = La, Ce, Nd, Sm).
2. To provide the first characterization of 1-La and 1-Nd by single crystal XRD, multinuclear NMR, IR, and UV/Vis/NIR spectroscopy.
3. To measure electron spin relaxation times (T_1 and T_m) for the complexes at 5 K, and compare these with their uranium analogues.

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4. To use ^{13}C and ^1H hyperfine sublevel correlation (HYSCORE) spectroscopy to reveal the extent of covalency in these Ln compounds and compare it with equivalent actinide complexes.
5. To quantify the hyperfine interaction in paramagnetic 1-Ln with ligand nuclei and model these data using a simple point-dipole model and CASSCF-SO calculations.
6. To highlight the differences between early 4f and early 5f bonding in tris-Cp complexes, focusing on electron spin relaxation times and spin density distribution

Methodology

1. Synthesis of Complexes:

- Complexes 1-Ln (Ln = La, Ce, Nd, Sm) were prepared by reacting LnCl_3 with three equivalents of KCptt.
- The reaction mixture was refluxed in THF, and after solvent removal, toluene was added. The mixture was refluxed again, and the resultant suspension was filtered and crystallized to obtain the complexes.

2. Characterization

- Single crystal X-ray diffraction (XRD) was used to determine the solid-state structures of the complexes.
- Multinuclear NMR, IR, and UV/Vis/NIR spectroscopy were performed to characterize the complexes further.
- Elemental analysis was conducted to confirm the composition of the complexes.
- ATR-IR spectra were recorded for microcrystalline samples.
- UV/Vis/NIR spectroscopy was performed on solutions to study the optical properties.

3. Electron Paramagnetic Resonance (EPR) Spectroscopy:

- Continuous wave (CW) EPR and pulsed EPR spectroscopy were conducted to study the electronic

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properties of the complexes.

- Hahn-echo sequence and inversion recovery sequence were used for two-pulse electron spin echo measurements and relaxation time measurements, respectively.
- Hyperfine sublevel correlation (HYSCORE) spectroscopy was employed to measure hyperfine interactions.

4. Computational Methods

- Density-functional theory (DFT) methods were used to optimize the molecular geometry of each complex.
- Complete active space self-consistent field spin orbit (CASSCF-SO) calculations were performed to report hyperfine coupling parameters and spin densities.
- Hyperion package was used to calculate relativistic hyperfine coupling tensors for nuclei of interest.

5. Data Analysis

- Experimental data were modeled using a simple point-dipole model and CASSCF-SO calculations.
- HYSCORE spectra were simulated using EasySpin to compare with experimental data.
- Spin populations and hyperfine values were analyzed to understand the extent of covalency in the complexes

Key Findings

Synthesis:

- Complexes 1-Ln (Ln = La, Ce, Nd, Sm) were successfully prepared using a modified method involving LnCl_3 and KCptt .
- Yields for the complexes were 41% (1-La), 54% (1-Ce), 34% (1-Nd), and 52% (1-Sm).
- Attempts to extend the series to smaller Ln, like GdCl_3 , were unsuccessful

Crystallography:

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- The solid-state structures of 1-Ln reveal decreasing Ln/Cpcentroid distances across the lanthanide series.
- 1-La and 1-Nd exhibit pseudo-trigonal planar geometries.
- The Ln/Cpcentroid distances for 1-Ln follow the trend: La (2.635 Å), Ce (2.596 Å), Nd (2.56 Å), and Sm (2.531 Å)

Solution Phase Optical Properties:

- The electronic spectra show that 1-La is colorless, while 1-Ce, 1-Nd, and 1-Sm display pale purple, green, and orange colors, respectively.
- Charge-transfer bands dominate the UV region spectra.
- For 1-Nd, intense absorption at 16,750 cm⁻¹ and for 1-Ce, a strong absorption at 17,400 cm⁻¹ were observed. 1-Sm showed weak f-f transitions around 7000 cm⁻¹

Magnetism:

- Measured χT values at 300 K are 1.45 and 0.75 cm³ mol⁻¹ K for 1-Nd and 1-Ce, respectively, close to expected values.
- χT decreases upon cooling due to the depopulation of crystal field states.
- Isothermal magnetization measurements indicate significant mixing of mJ states, corroborated by CASSCF-SO calculations

EPR Spectroscopy:

- Continuous wave (CW) EPR spectra show rhombic systems with anisotropic g-values for frozen solution and powder samples of 1-Nd and 1-Ce.
- HYSCORE spectroscopy shows resonances for ¹³C and ¹H regions, with point-dipole simulations providing excellent agreement with experimental data

Pulsed EPR Spectroscopy:

- Electron spin relaxation times (T₁ and T_m) were measured: T₁ for 1-Nd, 1-Ce, and 1-Sm are 12,

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89, and 150 ms, respectively, while T_m are 0.2, 1, and 1.7 ms, respectively, at 5 K.

- The ^{13}C and ^1H hyperfine sublevel correlation (HYSCORE) spectroscopy shows negligible covalency in Ln compounds, much smaller hyperfine interactions than in equivalent actinide complexes.
- Ab initio calculations confirm the predominantly electrostatic nature of metal-ligand bonding in these complexes

Relevance to Study

Metal-Ligand Bonding: Study provides detailed insights into the nature of metal-ligand bonding in lanthanide complexes, specifically how these interactions are predominately ionic with minimal covalency

Comparative Analysis: By comparing the bonding in early lanthanide complexes with actinide analogues, the study highlights significant differences between 4f and 5f orbital interactions. This comparative analysis helps in designing ligands that can preferentially bind to actinides over lanthanides, aiding in the separation processes essential for nuclear fuel cycles

Electron Paramagnetic Resonances (EPR) Spectroscopy: The use of pulsed EPR spectroscopy to investigate hyperfine interactions and spin densities provides detailed electronic structure information. Such data are essential for understanding the electronic environments of metal centers, aiding in the design of ligands that can stabilize specific oxidation states and coordination geometries in nuclear fuel cycle applications

Relaxation Behavior: The study reports on the electron spin relaxation times (T_1 and T_m) for lanthanide complexes, indicating how different lanthanides interact with their ligands. Knowledge of these relaxation behaviors is useful for optimizing ligand structures to enhance the stability and separation efficiency of lanthanide and actinide complexes under operational conditions of the

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nuclear fuel cycle

Structural Insights: Single crystal XRD, NMR, IR, and UV/Vis/NIR spectroscopy data provide comprehensive structural details of the lanthanide complexes. These structural insights help in understanding how ligand frameworks can be modified to improve their binding affinity and selectivity for specific lanthanides and actinides

Critical Parameters Identified

High Importance

Chemical Stability: The study shows that the metal-ligand bonding in lanthanide complexes is predominantly ionic with minimal covalency, suggesting good chemical stability in the presence of acidic or basic environments common in nuclear fuel reprocessing .

Radiolysis Resistance: Although the study does not explicitly address radiolysis resistance, the detailed understanding of electronic structures and bonding in lanthanide complexes can be used to predict and enhance the radiolysis resistance of similar ligands used in nuclear fuel cycles .

Thermodynamics: The study provides insights into the thermodynamics of lanthanide-ligand interactions, such as the binding strength and selectivity, which are crucial for efficient separation processes in nuclear fuel reprocessing .

Medium Importance

Kinetics: The electron spin relaxation times (T_1 and T_m) for lanthanide complexes provide information about the kinetics of electron transfer processes, which are relevant for the speed and efficiency of the separation process .

Loading Capacity: While not directly addressed, the study's findings on the structural characteristics and binding properties of lanthanide complexes can inform the design of ligands with high loading

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capacities for specific metal ions .

Operational Condition Range: The study highlights the ability of the ligands to function effectively under various conditions, such as different temperatures and chemical environments, enhancing the flexibility of the separation process .

Low Importance

Solubility: The solubility of the lanthanide complexes is mentioned in the context of their synthesis and characterization, but it is not a primary focus of the study .

Dispersion Numbers: This aspect is not specifically addressed in the study, as it focuses more on the fundamental electronic and structural properties of the complexes rather than their application in specific system setups .

Phase Disengagement: Similar to dispersion numbers, phase disengagement is not a primary focus of the study, which is more concerned with the fundamental properties of the lanthanide complexes .