

Structures of Lanthanide Halide Cluster Anions Studied by Ion Mobility Mass Spectrometry: Relationship between Ionic Radius and Geometric Structure due to Lanthanide Contraction

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Lanthanoid (Ln) complexes are characterized by diverse coordination structures that are influenced by their ionic radii. The ionic radii of lanthanoid(III) ions (Ln^{3+}) gradually decrease from La to Lu, known as the lanthanoid contraction. It is well-established that this systematic reduction in ionic radius leads to diversity in coordination structures, highlighting a relationship between ionic size and coordination chemistry. Rutkowski's previous investigation into the coordination structures of lanthanoid chloride clusters using electrospray ionization (ESI) mass spectrometry and density functional theory (DFT) calculations showed that $\text{La}_6\text{Cl}_{19}^-$ and $\text{Lu}_6\text{Cl}_{19}^-$ are classified into different structural classes.¹ This study aims to elucidate the relationship between ionic radii of whole Ln and their cluster structures as coordination models, offering insights into the structural adaptability of lanthanoid systems, which were recently found to play roles in certain bacterial enzymes.² Lanthanoid chloride ions were generated by ESI, and their collision cross-sections (CCS) were measured using ion mobility mass spectrometry equipped with cyclic-type ion drift cells.³ The CCS analysis revealed that $\text{Ln}_6\text{Cl}_{19}^-$ clusters for Sm–Lu exhibit two distinct components corresponding to different isomers: an octahedral isomer and a prism-like isomer shown in **Fig**. In contrast, smaller clusters such as $\text{Ln}_5\text{Cl}_{16}^-$ and $\text{Ln}_4\text{Cl}_{13}^-$ displayed only one component, suggesting a single dominant structural configuration. The relationship between ionic radii and CCS values revealed a turning point in the structural trends of $\text{Ln}_5\text{Cl}_{16}^-$ and $\text{Ln}_4\text{Cl}_{13}^-$.

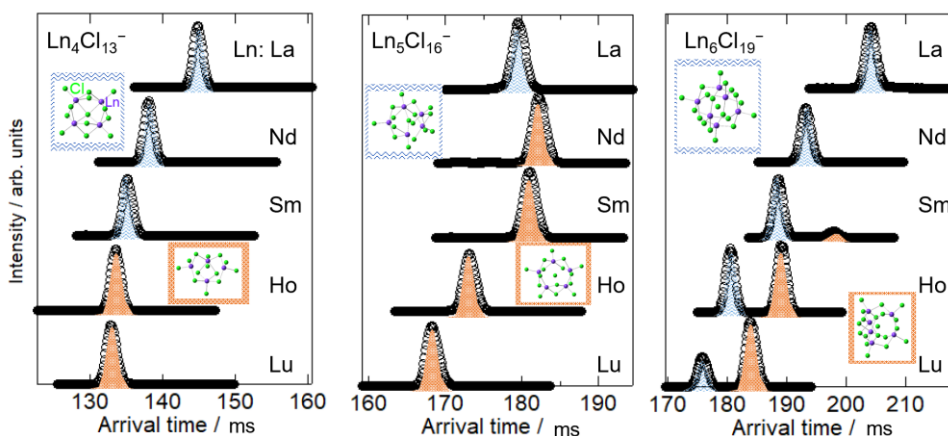


Fig: Arrival time distributions in ion mobility measurements and assigned structures.

1) P. X. Rutkowski et al, *Phys. Chem. Chem. Phys.* **2012**, 14, 1965. 2) Y. W. Deng et al, *J. Biol. Inorg. Chem.* **2018**, 23, 1037. 3) Y. Nakajima et al, *Phys. Chem. Chem. Phys.* **2025**, 27, 1017.