

Scientists show charged salts can extract specific central lanthanide elements

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Oak Ridge National Laboratory researchers made a molecule that could selectively bind to metals in the middle of the lanthanide series. The accomplishment proves selective extraction of central lanthanides is possible and eventually could provide future materials for technologies such as strong magnets in wind turbines. Credit: Oak Ridge National Laboratory, U.S. Dept. of Energy

Rare earth elements are metals used in technologies from wind turbines and magnetic resonance imaging agents to industrial catalysts and high-definition televisions. Most are lanthanides, elements with atomic number from 57 to 71, lanthanum to lutetium, in the periodic table. The lanthanides predominantly form trivalent cations (with a net positive charge of three). Lanthanides have similar chemical properties, and the only significant physical characteristic that distinguishes them from each other is size.

As lanthanides increase in atomic number, the radii of their ions decrease—a phenomenon known as the "lanthanide contraction." This contraction of ionic radius creates distinct chemical and

electronic properties for each element because the same charge is present but confined to a shrinking area.

Researchers at the Department of Energy's Oak Ridge National Laboratory wanted to find out if it was possible to make a molecule that could selectively bind to metal cations in the middle of the lanthanide series. The team provided a proof-of-principle by successfully creating a new ligand that selectively extracted central lanthanides. Easier accessibility to these central lanthanides could lead to advances in materials for technologies such as lasers (which employ the central lanthanides holmium and dysprosium), strong magnets (holmium), lights (dysprosium) and neutron-absorbing control rods in nuclear reactors (erbium).

Sheng Dai, who holds joint appointments at ORNL and the University of Tennessee—Knoxville, conceived of the novel approach to selectively extract central lanthanides. His group works with [ionic liquids](#), salts that are liquid at room temperature. Salts are neutral compounds that contain positive and negative ions. In a task-specific ionic liquid, a molten salt and a ligand are combined in the same molecule. Dai's team created a task-specific ionic liquid that uses charge density as the basis for discriminating between individual lanthanides.

"We've taken a ligand and tethered it to a positively charged ion," said Neil Williams of ORNL's Chemical Separations Group, who presented the research results on Dec. 19 in Honolulu at Pacificchem 2015. "We took a ligand that was selective for lutetium, at the end of the lanthanide series, and we made it selective for holmium, which is closer to the middle of the lanthanides. We've shifted this ligand's selectivity by tethering a [positive charge](#) to it."

Improved lanthanide selectivity opens the door to better extractions. "Before, you would have to go

through very time consuming separations requiring lots of stages to separate individual elements," Williams said. "Task-specific ionic liquids allow you to remove those stages and go directly after what you want."

New process, new possibilities

In traditional lanthanide separations, ligands that complex with lanthanides are mixed into an organic solvent and later mixed with an aqueous solution of the lanthanides. Like oil and water in salad dressing, organic and aqueous phases separate, and the ligand-bound lanthanide gets extracted into the organic phase.

Organic solvents have drawbacks. They are flammable, evaporate and can develop an intermediate phase that lowers the effectiveness of extractions. In the 1990s, scientists began exploring room-temperature ionic liquids as possible replacements for organic solvents.

A new approach ORNL researchers have taken employs a task-specific ionic liquid that adapts a common ligand, tetraoctyl diglycolamide (TODGA), which forms complexes with lanthanides. The scientists altered TODGA, making it a task-specific ionic liquid selective for binding to the central lanthanides, by removing two octyl [eight-carbon] chains and attaching an imidazolium, a positively charged ring containing three carbons and two nitrogens. These modifications changed the ligand's character. "We've gone from a ligand that was not charged to now having a ligand that has a positive charge," Williams explained. "That's what is driving our selectivity change."

Williams made the compounds and sought more efficient synthesis routes with University of Tennessee postdoctoral fellow Chi-Linh Do-Thanh. They purified compounds using automated column chromatography systems with silica gel columns and various [organic solvents](#) with different polarities to separate each reaction component and eventually obtain the final compound—the desired task-specific ionic liquid.

Huimin Luo of ORNL's Energy and Environmental Sciences Directorate, former ORNL postdoctoral

fellow Joseph Stankovich and Williams performed analyses to determine how effectively the task-specific ionic liquid separated individual lanthanides from each other. They used an inductively coupled plasma mass spectrometry, which breaks molecules in extracted samples into their elemental components with a plasma torch that is hotter than the surface of the sun. These individual charged elements are then identified based on their respective masses.

"When you have a metal that's really charge-dense and you have another ligand that comes to complex with it, or bind to it, and that's also similarly charged, you can have a repulsion of the two charges," Williams said. Charge repulsion decreases the effectiveness of [ligand](#) binding but improves selectivity. "It's a tradeoff, Williams said. "You don't pull out as much. But you selectively pull out what you want. That's why we are able to drive the selectivity from lutetium to holmium."

Next the scientists will alter other ligands to further explore the effect on selectivity and to study complexes using a wider variety of solvents. They also will investigate separating lanthanides from actinides, which are radioactive metals from [atomic number](#) 89 to 103 (actinium to lawrencium) including uranium, plutonium and thorium. Because lanthanides and actinides are produced in nuclear reactors, better separations of radioactive elements with short half-lives from those with longer half-lives could lower storage costs, Williams said.

Provided by Oak Ridge National Laboratory

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