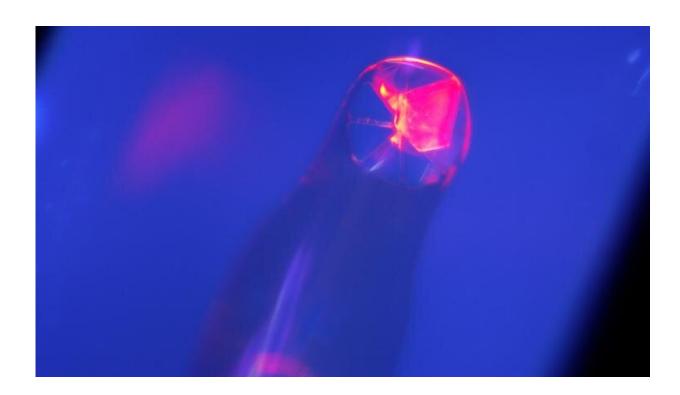


Developing new processes to examine some of the rarest and most toxic elements on Earth

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A new compound of curium (a radioactive, rare and costly element) photographed at LLNL during crystallography experiments. The team from LLNL and OSU used the so-called "polyoxometalate ligands" (POMs) to capture rare isotopes and form crystals big enough to be characterized, even when only 1-10 micrograms of the rare isotope are available. Crystals of this curium compound are uncolored under ambient light but glow intensely pink-red when exposed to ultraviolet light. Credit: Gauthier Deblonde/LLNL.



The synthesis and study of radioactive compounds are naturally difficult due to the extreme toxicity of the materials involved, but also because of the cost and scarcity of research isotopes.

Now, Lawrence Livermore National Laboratory (LLNL) scientists and their collaborators at Oregon State University (OSU) have developed a new method to isolate and study in great detail some of the rarest and most <u>toxic elements</u> on Earth. The research appears in *Nature Chemistry*.

Traditional synthetic methods and chemical studies focus on small inorganic or organic complexes of the studied isotope and typically require several milligrams of sample per attempt. Milligram quantities may not sound like a lot, but for some isotopes this is equivalent to the world's yearly supply. Some radioisotopes also are too costly, too short-lived or too toxic to be studied with current methods, leaving them out of reach for detailed chemical studies.

In the new research, the team demonstrated that by leveraging fundamental chemical properties, such as molecular weight and solubility, it is possible to synthesize coordination compounds of rare/toxic/radioactive/precious elements and characterize them in great detail, while using very tiny amounts, down to the microgram scale. The new method requires more than 1,000 times less material than prior state-of-the art approaches, representing a groundbreaking tool to advance knowledge of the most difficult-to-study elements on Earth.

The newly proposed approach could be used to discover and study many new compounds containing rare isotopes, such as actinides and radiolanthanides—allowing scientists to unravel bonding trends and possibly isotopic trends in the periodic table. It also offers a viable path to isolate compounds and study the chemistry of elements that have remained inaccessible with previous methods, such as actinium, transcalifornium elements and more.



"The simplicity, efficacy and modularity of the newly proposed method are astonishing, and it significantly decreases the <u>radiation exposure</u> to workers, preserves the nation's isotope resources and drastically cuts costs," said LLNL scientist and project lead Gauthier Deblonde.

The method involves heavy polyoxometalate ligands (POMs) and enables the simple formation, crystallization, handling and detailed spectroscopic and structural characterization of complexes containing rare isotopes starting from just 1–10 micrograms. Several new single crystal X-ray diffraction structures were found, including three new compounds of curium. For context, curium isotopes are not only radiotoxic, but they also are rare and extremely expensive, to a point where just 10 curium complexes had been isolated and characterized by single crystal X-ray diffraction since the discovery of this element in 1944. The new approach also yielded the very first experimental measurement of the 8-coordinated ionic radius of the Cm³⁺ ion.

"The very nature of the materials involved in this research has its many limitations, but the new method overcomes them. Enough so that we can start to understand their chemistry and appreciate their beauty," said Ian Colliard, first author of the publication and OSU Ph.D. candidate at the time of the study (now a postdoctoral researcher at LLNL).

The study also revealed that POMs have very interesting properties compared to classic molecules. For example, the team realized that most POMs render curium ions (i.e., Cm³+) highly luminescent, offering a potential way for detecting them even at very low concentrations. The various curium-POM complexes tested exhibit strong fluorescence emission, in both the solid-state and solution-state. The POMs also form highly luminescent complexes with many other elements such as europium, terbium, dysprosium and samarium, offering a convenient way to study their chemistry.



"The team continues to apply our new POM-based approach to unlock the study of many novel actinide compounds and rare isotope materials, with more successes already in the pipeline," Deblonde said.

More information: Gauthier Deblonde, Polyoxometalates as ligands to synthesize, isolate and characterize compounds of rare isotopes on the microgram scale, *Nature Chemistry* (2022). DOI: 10.1038/s41557-022-01018-8. www.nature.com/articles/s41557-022-01018-8

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