The element of surprise

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Credit: AI-generated image (disclaimer)

Many of us are often told we bear a resemblance to another member of our family—for instance, that we have our mother's nose or our father's eyes.

Chemical elements on the periodic table also have family resemblances that could provide predictive insight into the way elements interact, leading scientists to not-yet-imagined applications.

In the case of one element, protactinium, chemical similarities produced by the configuration of its outermost electrons link two families of elements: the stable and well-known transition metals and the more exotic actinides.

In a new study from the U.S. Department of Energy's (DOE) Argonne National Laboratory and the University of Lille in France, chemists have explored protactinium's multiple resemblances to more completely understand the relationship between the transition metals and the complex chemistry of the early actinide elements.

Protactinium's principal value is not in its commercial uses, but in providing new fundamental insights into the chemistry of the elements. Protactinium is an actinide element and sits between thorium and uranium on the periodic table. However, protactinium also closely resembles niobium and tantalum, both of which are transition metals used in a range of chemical and metallurgical applications. When chemists understand their similarities in more detail, they may discover novel and yet-undiscovered applications for these and other related elements.

"Protactinium is at a fulcrum on the periodic table," said study author and Argonne chemist Richard Wilson. "The question of how we put together the periodic table really sits at the core of our thinking about protactinium."

The answer to whether protactinium acts more like an actinide or like a transition metal lies in a protactinium atom's outer electron shells. Scientists designate each shell with both a number (1 through 7) and a letter (s, p, d or f). Which shell an element's outer electrons inhabit, in terms of number and letter, defines its family and helps determine a broad range of its chemical and physical behavior.

The difference between the transition metals and the actinides lies in which outer shell gets filled first by available electrons. Protactinium, Wilson noted, is particularly important because it represents the boundary at which a 'd' orbital and an 'f' orbital change places energetically. This determines how the orbitals get filled and how they interact or bond with their neighbors.

"The 'd' orbitals in transition metals participate in chemical bonding in a very direct way, and they can organize into fairly predictable structures," Wilson said. "The actinides don't form the same kinds of bonds as readily."

According to Wilson, chemists studying actinides who have tried to coax protactinium to act like its transition metal cousins have encountered limited success. "Can we make protactinium behave like niobium and tantalum? The answer experimentally is 'not yet,'" Wilson said. "But working on the theory of this unique element could give us a new view on how it is able to sit right at this important chemical and energetic intersection."

The changes in electron orbitals and bonding behaviors that occur within the heavy elements only increase as the periodic table goes on. In the heaviest elements, Wilson said, relativistic effects begin to supersede our classical understanding of how certain elements "should" behave, even to the point at which a hypothesized element could resemble both an inert noble gas and a highly active metal at the same time.

"We're beginning to understand that protactinium is the doorstep upon which bonding in the periodic system is starting to change," Wilson said. "We're drilling down to what really makes the periodic table tick."

The study, "Protactinium and the intersection of actinide and transition metal chemistry," appeared in the February 12 online issue of *Nature*

Communications.

More information: Richard E. Wilson et al, Protactinium and the intersection of actinide and transition metal chemistry, *Nature Communications* (2018). DOI: 10.1038/s41467-018-02972-z

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