

Striking rare gold: Researchers unveil new material infused with gold in an exotic chemical state

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Structure of the gold-halide perovskite. The elongated gold-chloride octahedra, composed of gold (Au) surrounded by six neighboring chlorine (Cl) atoms, are shaded in the structure: burnt-red octahedra represent Au²⁺-chloride and gold octahedra represent Au³⁺-chloride. Turquoise spheres represent cesium (Cs) atoms, and light- green spheres represent chlorine (Cl) atoms. The inset shows the shortest gold-chloride bonds. Credit: Karunadasa et al. 2023.



For the first time, Stanford researchers have found a way to create and stabilize an extremely rare form of gold that has lost two negatively charged electrons, denoted Au^{2+} . The material stabilizing this elusive version of the valued element is a halide perovskite—a class of crystalline materials that holds great promise for various applications including more-efficient solar cells, light sources, and electronics components.

Surprisingly, the Au²⁺ <u>perovskite</u> is also quick and simple to make using off-the-shelf ingredients at <u>room temperature</u>.

"It was a real surprise that we were able to synthesize a stable material containing Au²⁺—I didn't even believe it at first," said Hemamala Karunadasa, associate professor of chemistry at the Stanford School of Humanities and Sciences and senior author of the study published Aug. 28 in *Nature Chemistry*. "Creating this first-of-its-kind Au²⁺ perovskite is exciting. The gold atoms in the perovskite bear strong similarities to the copper atoms in high-temperature superconductors, and heavy atoms with unpaired electrons, like Au²⁺, show cool magnetic effects not seen in lighter atoms."

"Halide perovskites possess really attractive properties for many everyday applications, so we've been looking to expand this family of materials," said <u>Kurt Lindquist</u>, the lead author of the study who conducted the research as a Stanford doctoral student and is now a postdoctoral scholar in <u>inorganic chemistry</u> at Princeton University. "An unprecedented Au²⁺ perovskite could open some intriguing new avenues."

Heavy electrons in gold



As an elemental metal, gold has long been valued for its relative scarcity as well as its unmatched malleability and chemical inertness—meaning it can be easily shaped into jewelry and coins that do not react with chemicals in the environment and tarnish over time. An additional key reason for its value is gold's namesake color; arguably no other metal in its pure state has such a distinctively rich hue.

The <u>fundamental physics</u> behind gold's acclaimed appearance also explains why Au^{2+} is so rare, Karunadasa explained.

The root reason is <u>relativistic effects</u>, originally postulated in Albert Einstein's famed theory of relativity. "Einstein taught us that when objects move very fast and their velocity approaches a significant fraction of the speed of light, the objects get heavier," Karunadasa said.

This phenomenon applies to particles, too, and has profound consequences for "massive" heavy elements, such as gold, whose <u>atomic</u> <u>nuclei</u> boast a large number of protons. These particles collectively exert immense positive charge, forcing negatively charged electrons to whirl around the nucleus at breakneck speeds. As a consequence, the electrons grow heavy and tightly surround the nucleus, blunting its charge and allowing outer electrons to drift farther than in typical metals. This rearrangement of electrons and their energy levels leads to gold absorbing blue light and therefore appearing yellow to our eye.

Because of the arrangement of gold's electrons, thanks to relativity, the atom naturally occurs as Au^{1+} and Au^{3+} , losing one or three electrons, respectively, and spurning Au^{2+} . (The "2+" indicates a net positive charge from the loss of two negatively charged electrons, and the "Au" chemical symbol for gold hails from "aurum," the Latin word for gold.)

A squeeze of vitamin C



With just the right molecular configuration, Au^{2+} can endure, the Stanford researchers found. Lindquist said he "stumbled upon" the new Au^{2+} -harboring perovskite while working on a broader project centered on magnetic semiconductors for use in electronic devices.

Lindquist mixed a salt called cesium chloride and Au^{3+} -chloride together in water and added <u>hydrochloric acid</u> to the solution "with a little vitamin C thrown in," he said. In the ensuing reaction, vitamin C (an acid) donates a (negatively charged) electron to the common Au^{3+} forming Au^{2+} . Intriguingly, Au^{2+} is stable in the solid perovskite but not in solution.

"In the lab, we can make this material using very simple ingredients in about five minutes at room temperature," said Lindquist. "We end up with a powder that's very dark green, nearly black, and is surprisingly heavy because of the gold it contains."

Recognizing that they may have hit new chemistry paydirt, so to speak, Lindquist performed numerous tests on the perovskite, including spectroscopy and X-ray diffraction, to investigate how it absorbs light and to characterize its crystal structure. Stanford research groups in physics and chemistry led by Young Lee, professor of applied physics and of photon science, and Edward Solomon, the Monroe E. Spaght Professor of Chemistry and professor of photon science, further contributed to studying the behavior of Au^{2+} .

The experiments ultimately bore out the presence of Au^{2+} in a perovskite and, in the process, added a chapter to a century-old story of chemistry and physics involving Linus Pauling, who received the Nobel Prize in Chemistry in 1954 and the Nobel Peace Prize in 1962. Early in his career, he worked on <u>gold</u> perovskites containing the common forms Au^{1+} and Au^{3+} . Coincidentally, Pauling also later studied the structure of vitamin C—one of the ingredients required to yield a stable perovskite



containing the elusive Au^{2+} .

"We love Linus Pauling's connection to our work," Karunadasa said. "The synthesis of this perovskite makes for a good story."

Looking ahead, Karunadasa, Lindquist, and colleagues plan to study the new material further and tweak its <u>chemistry</u>. The hope is that an Au^{2+} perovskite can be used in applications that require magnetism and conductivity as electrons hop from Au^{2+} to Au^{3+} in the perovskite.

"We're excited to explore what an Au²⁺ perovskite could do," Karunadasa said.

More information: Kurt P. Lindquist et al, Stabilizing Au2+ in a mixed-valence 3D halide perovskite, *Nature Chemistry* (2023). DOI: 10.1038/s41557-023-01305-y

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