Thorium lends a fiery hand

John Arnold, **Thomas L. Gianetti** and **Yannai Kashtan** look back on thorium's chemistry, and look forward to harnessing its nuclear potential.

ALEX WING

In 1828, the chemist Jöns Jacob Berzelius received for inspection an unusual ore, which he named thoria, after Thor, the Scandinavian god of thunder and war. The metal later isolated from it was named thorium, which has persisted to the present day, even though the ore has changed its name slightly to thorite. Although natural thorium is radioactive, almost all of its present uses exploit its chemical, rather than its nuclear, properties.

The first practical use for thorium was found 63 years after Berzelius's discovery. Carl Auer von Welsbach found that a 'mantle', made of 99% ThO_2 and 1% CeO_2, surrounding a gas flame would radiate white light more efficiently than an open flame, and this gas-lamp technology quickly spread throughout Europe. Although these lamps have since been superseded, thorium compounds are still used today as catalysts for petroleum cracking, sulfuric acid synthesis and in the Ostwald process for nitric acid synthesis. Thorium also features, because of its strength and creep resistance at high temperatures, in the Mag–Thor alloy used in aircraft and rocket engines. Additionally, ThO_2 has a high refractive index and low dispersion and is therefore used in high-quality optical lenses[1].

Among its remarkable chemical and physical properties, thorium metal is liquid over the widest temperature range of any element, and ThO_2 has the highest melting point of any known oxide[2]. Being the first true actinide, thorium still has an empty 5*f* orbital, and therefore Th(IV) is the most stable and plentiful oxidation state. Because of its large size, thorium's coordination chemistry is also quite remarkable, with $Th(NO_3)_4{\cdot}5H_2O$ being the first recorded example of an 11-coordinate complex[3]. Additionally, Th(III) is also an accessible oxidation state and has been reported[4] as free Th^{3+} in an aqueous solution of $ThCl_4$ and HN_3. Ligand-stabilized Th(III) complexes are also known and include $ThCp_3$ and the bis(trimethylsilyl) Cp analogue[5]. Interestingly, experimental and computational evidence suggests the single unpaired electron in the $ThCp_3$ complex resides not in a 5*f* orbital, but in the $6d_{z^2}$ (refs 6,7). Unfortunately, despite the existence of a formally trivalent species, no redox chemistry has yet been observed with thorium.

Recent research has led to promising thorium-based materials — such as thorium- and copper-doped magnetite — to catalyse the activation of small molecules. These materials could eventually replace the more traditional chromium- and copper-doped magnetite catalysts used to form carbon dioxide and hydrogen from carbon monoxide and water[8]. Along similar lines, several research groups have synthesized well-defined thorium complexes to study their bonding and reactivity. Recent reports include the synthesis and characterization of thorium complexes using corrole ligands[9] and a dihalide thorium complex supported by trans-calix[2]benzene[2]pyrrolide, which on reduction undergoes double aryl metallation of the ligand[10].

Although most of the current research is focused on its chemical characteristics, perhaps thorium's most revolutionary potential use involves its nuclear chemistry. The theoretical feasibility of a thorium-based nuclear reactor has long been recognized. However, technical difficulties as well as prioritized interest in uranium reactors (which some posit stems from uranium reactors' greater ability to breed plutonium for fission bombs) have prevented the development of commercial thorium reactors. Natural thorium is almost exclusively ^{232}Th, thus no costly isotopic enrichment process would be necessary, and this would present a significant potential benefit over today's uranium-based reactors.

Perhaps the biggest advantages of thorium reactors are their safety and their relatively reduced environmental impact. Unlike uranium-based reactors, which produce waste that remains harmful for thousands of years, 83% of waste from a proposed liquid fluoride thorium reactor will become safe within 10 years, and the remaining 17% after 300 years. Thorium reactors aren't just an abstract concept either: the Indian government has a strong interest in thorium power because India has approximately a third of the world's thorium reserves, and in 2002 the government issued approval to start construction of a prototype thorium fast-breeder plant.

Thorium has proved itself as a catalyst and a great refractive material. With the effects of global climate change increasing with every passing year, hopefully more research and allocated resources will help thorium realize its great untapped potential and become a truly revolutionary material in our energy economy. ❐

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