Rounding up lutetium

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Rounding up lutetium

Lars Öhrström suspects that as time goes by, we may see more of lutetium — the last of the lanthanoids.

"We'll always have Paris" Rick says to Ilsa in their final goodbye on the foggy airstrip of Casablanca in the eponymous film. However, the question among chemists about the element lutetium, named after Lutetia, as the French capital was known in Roman times, is not so much about having it (it is more abundant than silver in the Earth's crust), but rather where to place it on the map.

With its valence electron configuration [Xe]$4f^{14}6s^25d^1$, element 71 seems to belong to group 3, but we often see it placed at the very end of the lanthanoid series. Its downstairs neighbour lawrencium, for which experimental data are much more difficult to obtain, is in the same ambiguous situation. So which elements should come below scandium and yttrium — lutetium and lawrencium, or lanthanum and actinium?

Many periodic tables — including the one presented by the International Union of Pure and Applied Chemistry (IUPAC) — are a bit vague on this point, and the question of group-3 membership is currently under thorough investigation by an IUPAC project[1]. Meanwhile, the chemical closeness of the group-3 and 4*f* blocks are widely recognized and reflected through collective names approved by the IUPAC: the 'lanthanoids' designate the 15 elements from lanthanum to lutetium, and the 'rare-earth metals' include those 15 as well as the unambiguous members of group 3, scandium and yttrium.

In any case, lutetium was isolated independently by three chemists in 1907, from samples composed of mainly an oxide of ytterbium, one of the later lanthanoids — so it seems fitting for lutetium to also be considered part of this gang. There appears to have been a heated argument over priority between two of the discoverers, Georges Urbain and Carl Auer von Welsbach, from France and Austria, respectively. The third — uncharacteristically for the field — kept a low profile, though the US chemist Charles 'King' James now has a National Historic Chemical Landmark dedicated to him at the University of New Hampshire.

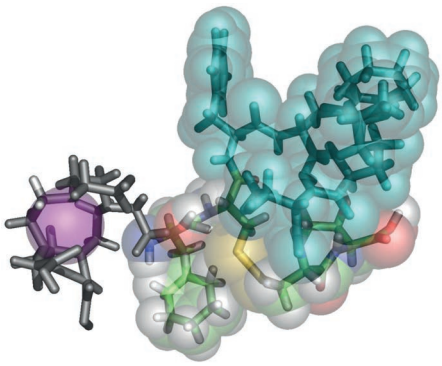

Illustration of a radiolabelled somatostatin analogue built using PyMOL (https://pymol.org) with a DOTA derivative (PDB: 1NC2[6], shown in black) enclosing lutetium (in lilac), and Tyr^3-octreotate (PDB: 1YL8[7]); the part of octreotate that binds to the receptor is shown in turquoise. PDB, protein data bank.

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The International Atomic Weights Commission under its chair Frank Clarke settled the dispute in 1909. The discovery credit was attributed to Urbain and his suggested name — lutecium, later to be spelled lutetium — was adopted over Welsbach's cassiopeium. Oddly, this was not the end of element 71's role in the naming game. In 2009, the name copernicium was proposed for the new element 112, but its suggested symbol Cp was rejected by IUPAC because it had already been used for cassiopeium — which, although not official, was used in the German-speaking world for a long time; copernicium instead got the symbol Cn.

Lutetium is mined together with the other rare-earth metals from oxides, but is much less abundant, with an average yield that is in the range 0.01–1.00%. Water solutions will contain colourless Lu^{3+} ions, the only stable oxidation state, with seven to nine water molecules coordinated. This means that to be useful, coordinating ligands need to support high coordination numbers, and that is exactly the case for motexafin (based on the 'texaphyrins'), a sub-class of porphyrin-like macrocycles with five instead of four nitrogen atoms in an approximately planar ring. Motexafin lutetium, which features Lu^{3+} and two acetate counter-ions coordinated on either side of the macrocycle, is potentially a good photosensitizer in dynamic phototherapy and has been going through phase I trials against prostate cancer[2].

Uses of the naturally occurring element are otherwise scarce, but its isotope Lu-177 is successfully used in experimental and clinical treatments against some severe cancers by hooking it up to a tetraazacyclododecane-tetraacetate (DOTA) ligand grafted to octreotate, a small peptide (pictured). DOTA acts as a seven- or eight-coordinating chelator whereas octreotate binds to receptors on the surfaces of a number of neuroendocrine tumour cells, thus directing the ionizing radiation of the lutetium isotope into the tumour and killing it[3,4].

Lutetium is also used, together with hafnium, in geological radioactive dating, and trace amounts can be analysed by neutron activation. This was recently used in quantifying rare earths, including lutetium, in the sediments of the Bou Regreg River in Morocco — not far from Casablanca[5]. Here's looking at Lu, kid! ❐

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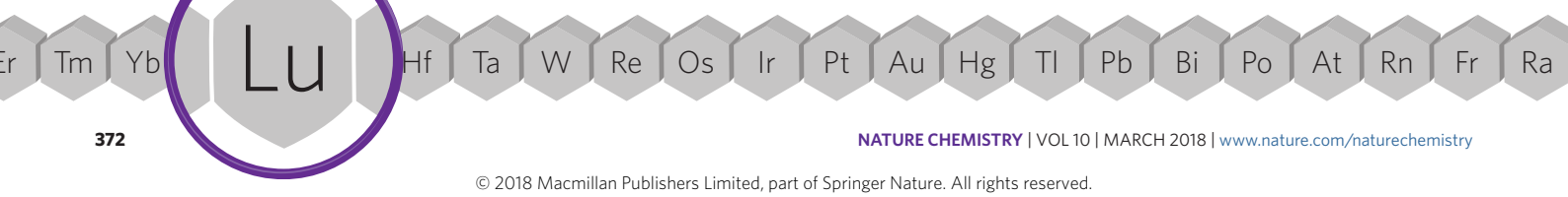

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