Controversy continues on the position of elements in the Periodic Table

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The International Union of Pure and Applied Chemistry (IUPAC) is all set to celebrate 2019 as the year of the Periodic Table of elements, the single most important organizational tool in chemistry[1]. While the central role of the Table in chemistry is undisputed, the debate on placement of elements in its various blocks has not settled even after 150 years. Though there is general agreement about the four blocks of the Table, there are many points to debate. The first element itself had options. The logic of keeping hydrogen simultaneously above Li and F is easy to understand. So was the debate to keep He above Be, and, also above Ne. IUPAC adopted to keep H above Li and He above Ne. The philosophical implications of the evolutionary changes in the Periodic Table have been discussed in detail by many, Eric Scerri prime among them[2].

Position of the first and last elements of the two f-blocks has been the subject of extensive discussion. The study of the artificial element Lr led to the suggestion that it should find a place in the Group 3 (ref. 3). Jensen[4] had summarized the continuing arguments[5] for and against placing Lu and Lr below Sc and Y, leaving the Lanthanides (La–Yb) and actinides (Ac–No), each block with 14 elements, below the d-block. These arguments included the ground state electronic configuration of Lu ($[Xe]4f^{14}5d^{1}6s^{2}$) and a comparison of ionization energies, and their similarity to Sc and Y. Scerri[6] had been passionate to advocate the same position. La and Ac in comparison, have less to lose by getting away from Sc and Y, to head the lanthanide and actinide series, even though the Royal Society of Chemistry had placed them below Sc and Y, with two 14-atom f-block rows Ce–Lu and Th–Lr (refs 5, 7). The ground state electronic structure of Lr is shown to be ($[Rn]5f^{14}7s^{2}7p^{1}$), not consistent with group 3, instead of ($[Rn]5f^{14}6d^{1}7s^{2}$) (ref. 8). IUPAC has played it safe by keeping two vacant positions below Sc and Y, with separate 15-atom rows of lanthanides and actinides[9]. The American Chemical Society has accepted this for its Periodic Table for the wall[10]. While this is an attractive solution, a beginning student of chemistry will be hard-pressed to accept that there are 15 and not 14 elements in the f-block.

The issue has come to focus again with the recent article of Ghanty and co-workers[11] from the Homi Bhabha National Institute, Mumbai. They have selected to study the four atoms and their ions encapsulated in Zintl ions Pb_{12}^{2-} and Sn_{12}^{2-} ($M@Pb_{12}^{2-}$ and $M@Sn_{12}^{2-}$, $M = Lr^{n+}$, Lu^{n+}, La^{n+}, Ac^{n+} and $n = 0$, 1, 2, 3) using density functional theory to get further insight to place the atoms in the transition metal group or in the f-block. The Zintl ions which satisfy the Wade's Rule are thought to provide a uniform environment for these atoms/ions.

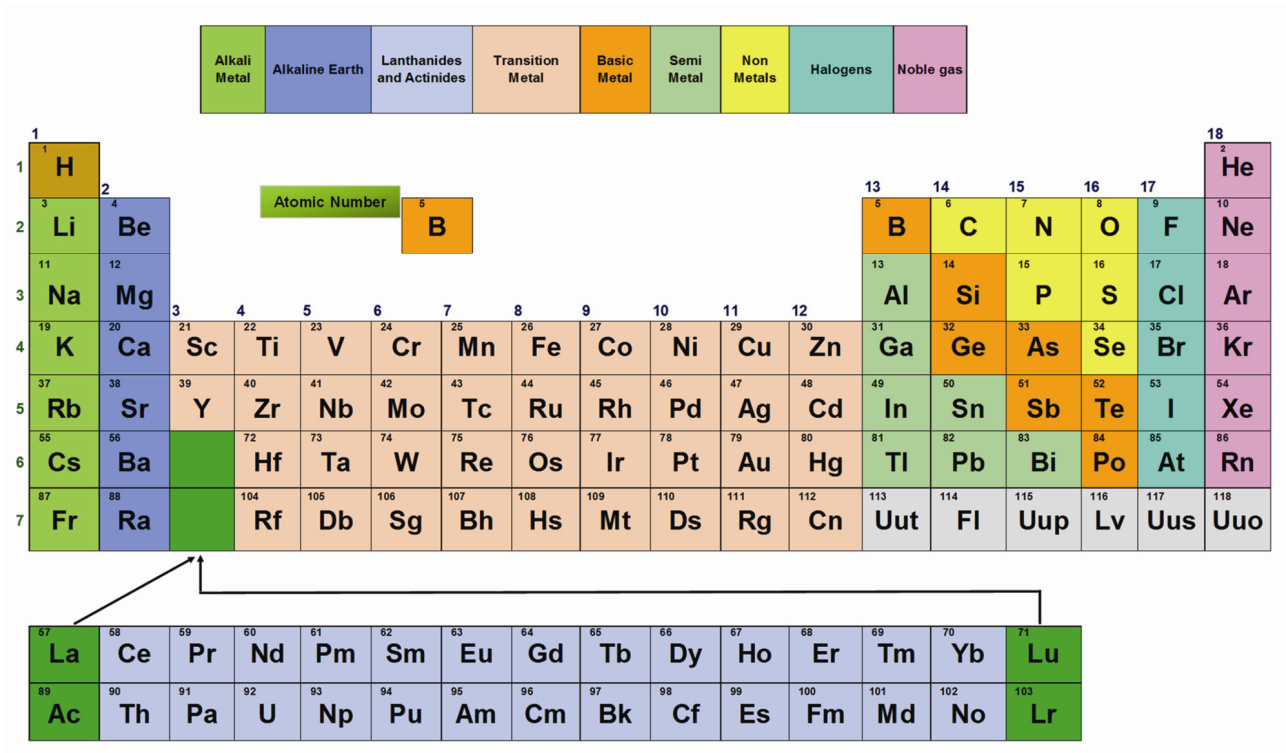

Figure 1. The two vacant slots below Y have four takers – La and Ac, as well as Lu and Lr (Table courtesy: Sagar Ghorai (Graduate Student, Inorganic and Physical Chemistry, IISc)).

Several structural and bonding parameters of these encapsulated complexes such as bond length, electron density variation, ionization potential, HOMO energy, HOMO–LUMO gap, thermodynamic stability, etc. were calculated and compared for Lr^{n+} and Lu^{n+}, especially for $n = 3$. These were found to be similar. In addition, corresponding values obtained for encapsulated La and Ac were also comparable. This has led the authors to suggest that if Lr and Lu are to be in the f-block, La and Ac also belong there. Thus they support IUPAC's 15-element f-blocks, however inconsistent it is with the 14-element upper limit of occupancy of f-block.

It is clear that this is not the last word of the debate. Already Lavalle has commented that the results of Ghanty *et al*. not only point out the similarities of La, Ac, Lu and Lr, but also their differences with rest of the lanthanides and actinides[12]. Thus the reasons for keeping all of them in the two 15-element f-blocks are not all that sound. There are further complications in any of these formulations. Many examples exist where the actinides act as though they are similar to transition metals, while lanthanides behave similar to the main group. Ligands could be designed to change these behaviours. Atomic properties of the four elements do not define the rest of their chemistry, or of the remaining f-block elements. Should the two positions be divided further so that the four elements are placed in them, La and Lu between Ba and Hf, and, Ac and Lr in between Ra and Rf (Figure 1)? The debate on the placement of elements in the Table is sure to continue.

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9. https://iupac.org/what-we-do/periodic-table-of-elements/
10. https://www.acs.org/content/acs/en/education/whatischemistry/periodictable.html; However there are other products available from ACS with different placement of atoms.
11. Joshi, M., Chandrasekar, A. and Ghanty, T. K., *Phys. Chem. Chem. Phys*., 2018, doi:10.1039/c8cp01056k. The introduction to this article gives a summary of the issues involved.
12. https://www.chemistryworld.com/news/new-rationale-for-15-element-wide-fblock/3009047.article (by Walshe, A., 2018, and comment by Lavalle, L.).

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