The Lewis octets and the Langmuir 18-electron (18e) rule are well-known principles in inorganic chemistry [1]. The key point is that, up to 18e, s-, p-, and d-like orbitals of the total system are fully occupied. The next step would be adding an f-like shell with 14 further electrons, giving a total of 32 electrons. If any f-contributions are desired at a central atom, an actinide is required. We first predicted from quantum chemical calculations that this could, indeed, be achieved in the isoelectronic series of icosahedral Pu@Pb$_{12}$ [2]. Other cases, identified by us, are the isoelectronic series of U@C$_{28}$ [3] and the case Pu@Sn$_{12}$ [4]. Before being able to claim the 32-electron rule as a chemical principle, it is desirable to have further examples. A new case reported is based on an actinide (U, Np, Pu, Am and Cm), doping a cage of silicon, Si$_{20}$ [5]. The stability of the charged systems is energetically favored by chemical bonding between the central atom and the Si cage supported by energy partitioning and topological analyses [6,7]. One neutral 32-electron system is also presented by adding two electron-donor lanthanide atoms on the pentagonal faces of the Si$_{20}$ cage. Combined with appropriate hexahedral electron donor atoms, the existence of this very stable silicon-based family suggests that it should be possible to create Si-based clusters containing early actinides, and to assemble further structures from them.

Our purpose here is to cover the recently discussed 32e compounds [8] and theoretically predicted as very stable species that should be accessible experimentally. The future will show how many 32e systems will turn up.

References