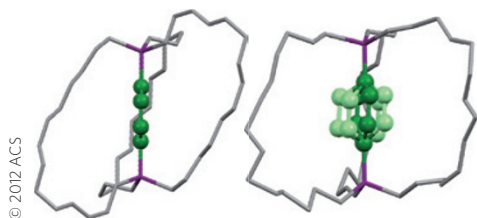


MOLECULAR MACHINES

Intracrystalline inflation

J. Am. Chem. Soc. **134**, 12458–12461 (2012)



There is much interest in the design of functional materials from the bottom up, so that their properties can be directly related to their molecular structures. Recently, a number of materials have been reported in which the properties depend on the control of motion within individual molecules. Now, Wataru Setaka and Kentaro Yamaguchi from Tokushima Bunri University in Japan have reported a compound that they describe as a ‘molecular balloon’, which ‘inflates’ when the temperature is increased.

These researchers have previously reported the synthesis of a molecular gyrotop — a system in which a phenylene rotor could freely rotate inside a cage formed by three long alkyl loops. The molecular balloon that they now describe was discovered when studying an intermediate structure in that prior synthesis. The alkyl-chain cage was constructed using ring-closing metathesis — producing a cage in which each chain contains an alkene. In contrast to the saturated alkyl cage of their original gyrotop — which is approximately spherical — an X-ray crystal structure of this compound (at 100 K) showed a cage that was ‘dented’ with the alkenyl chains collapsed inwards.

Analysis of the line shapes in the ^2H NMR of a deuterium-labelled version of this gyrotop enabled Setaka and Yamaguchi to estimate the rotation rate of the phenylene rotor. At low temperatures (<300 K), the phenylene ring flips slowly because its rotation is hindered by the collapsed cage structure. When the temperature was raised above 310 K, however, continuous rotation was observed.

To investigate the origin of this temperature-dependent behaviour the researchers performed a high-temperature X-ray crystallographic analysis. As expected, free rotation of the phenylene at high temperature results in a disordered structure in the centre of the cage. In addition, however, at this temperature the cage is inflated — apparently to avoid the steric clash with the rotor. The effect of this inflation is also seen in the macroscopic properties of the crystal — when the cage is inflated, the density of the unit cell is dramatically reduced. SD

‘ON WATER’ CHEMISTRY

Interfacial understanding

Angew. Chem. Int. Ed. **51**, 7981–7984 (2012)

Whereas nature chose water as the solvent to carry out the reactions necessary for life, chemists tend to choose organic media and even go to great lengths to make sure that they are working under dry conditions. One of the reasons for not using water is simple:

CLUSTER CHEMISTRY

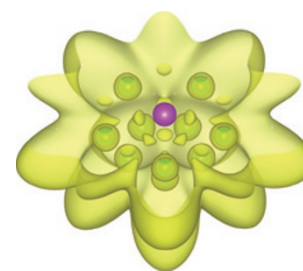
Filling in the blanks

Fully occupied orbitals endow compounds with particular stability — the Lewis 8-electron octet and the Langmuir 18-electron rule, which correspond to filled s , p and s , p , d orbitals, respectively, are firmly established. By the same token, it seems that 32-electron systems should be stable by virtue of their additional 14 electrons (the capacity of the f orbitals). Although $4f$ shells of lanthanides are too compact to allow the construction of 32-electron systems, the more diffuse $5f$ shells of the actinides have proven suitable. In previous work, 32-electron bonding has been proposed for endohedral clusters in which an actinide occupies the central cavity of a ligand cage, for an isoelectronic series based on $\text{U}@C_{28}$ and another based on $[\text{Pu}@M_{12}]^{2-}$ (where M is lead or tin).

In a separate study, another endohedral actinide@cage compound was characterized — an icosahedral silicon cage (Si_{20}) encapsulating a thorium atom. Noticing that $\text{Th}@Si_{20}$ falls short of fulfilling the 32-electron rule by only 8 electrons, a team of researchers from France and Finland led by Jean-Pierre Dognon and Pekka Pyykkö has now investigated its counterparts with heavier



actinides uranium, neptunium, plutonium, americium and curium. Calculations on these compounds revealed large binding energies — increasing from uranium to curium — that point to very stable actinide@ Si_{20} clusters (pictured). The actinides’ $7s$, $7p$, $6d$ and $5f$ electrons were found to participate in hybridization with the Si_{20} cage, in each case yielding an anionic 32-electron system. Furthermore, an analysis of the topology of electron densities — how electronic charges are distributed between two atoms, which provides an understanding of their bonding characteristics — also showed significant electron sharing occurred between actinide and silicon atoms.



These different analyses are all in agreement that notable covalency exists between the central actinides and the surrounding cages. Within this isoelectronic series, however, not all of the clusters have the same symmetry, and the plutonium- and americium-based structures were the most distorted. These findings provide significant support to the reliability of the 32-electron rule. Moreover, calculations also show that placing $[\text{U}@Si_{20}]^{6-}$ between two lanthanum centres leads to a neutral compound without disrupting its structure — which points to the possibility of further assembling actinide@ Si_{20} clusters into more complex architectures. AP

Chem. Sci. **3**, 2843–2848 (2012)