Endohedral [20]silafulleranes: valuable insights by $^{35}$Cl NMR spectroscopy


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Silafulleranes such as the parent siladodecahedrane $\text{Si}_{20}\text{H}_{20}$ have been an attractive subject of numerous purely quantum-chemical studies over decades.[1] Only in recent years have we found a one-step synthesis of the $T_h$-symmetric, Cl$^-$-encapsulating [20]silafullerane anion $[\text{Cl}@\text{Si}_{20}(\text{SiCl}_3)_{12}\text{Cl}]^- (\text{[1]}^-$, isolated as $[\text{nBu}_4\text{N}]\text{[1]}^-$; Fig. 1).[2] $[1]^-$ provides the starting point for different routes of regioselective derivatization: (i) desilylation of $[1]^-$ leading to the endohedral siladodecahedrane $[\text{Cl}@\text{Si}_{20}\text{H}_{20}]^- (\text{[2]}^-).[3]$ (ii) exhaustive substituent exchange on the Si$_{32}$ framework, and (iii) the one-step introduction of different substituents at the silyl groups and the cluster core of $[1]^-$ to obtain mixed-substituted derivatives such as $[\text{Cl}@\text{Si}_{20}(\text{SiH}_3)_{12}\text{Me}_8]^-(\text{[3]}^-)$.

The new silafulleranes bring together the fields of Si clusters and endohedral complexes: Due to their highly symmetric environments, the endohedral Cl$^-$ ions inside the Si$_{20}$ cages give rise to unusually narrow $^{35}$Cl NMR signals; their chemical shift values strongly depend on the exohedral substituents. A combined experimental and computational study rendered the $\delta(^{35}\text{Cl})$ value a useful probe for the Cl$^-\rightarrow\text{Si}_{20}$ interaction.[3] Consequently, $^{35}$Cl NMR spectroscopy on the Cl$^-$ guest gives valuable insights for the derivatization of the Si$_{20}$ host.

Figure 1: Crystallographically determined structures of selected silafullerane anions.

References