



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

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Silafullerenes 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]silafullerene anion $[\text{Cl}@\text{Si}_{20}(\text{SiCl}_3)_{12}\text{Cl}_8]^-$ (**[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 $[\text{Cl}@\text{Si}_{20}\text{H}_{20}]^-$ (**[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 $[\text{Cl}@\text{Si}_{20}(\text{SiH}_3)_{12}\text{Me}_8]^-$ (**[3]**⁻).

The new silafullerenes 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 $\text{Cl}^- \rightarrow \text{Si}_{20}$ interaction.^[3] Consequently, ^{35}Cl NMR spectroscopy on the Cl^- guest gives valuable insights for the derivatization of the Si_{20} host.

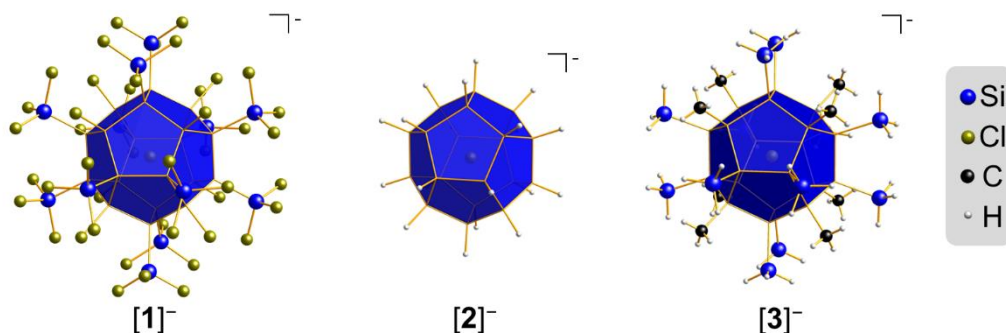


Figure 1: Crystallographically determined structures of selected silafullerene anions.

References

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