REVERSIBLE HYDROGEN ACTIVATION BY TRAPPED SILICON ANIONS

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Many interesting bonding modes are observable in the solid state but are not reproducible in solution. This disparity arises because crystal packing, particularly in ionic salts, provides substantial thermodynamic stabilisation that cannot typically be replicated in homogeneous media. In our recent work targeting anionic molecular group 2 hydride complexes,[1] we have discovered a soluble supramolecular assembly that mimics the solid-state environment for anions in ionic salts. The assembly positions four highly Lewis acidic metals (K and Ca) around an anion in a similar fashion to cations in crystal lattices (Figure 1).[2,3] As such, anions contained within this assembly experience similar stabilisation effects as they would in a solid-state lattice, thereby allowing solution-state stability of anions that are typically unstable in solution.

A demonstration of this stabilisation strategy is the isolation of the $[SiH_6]^{2-}$ anion in solution at room temperature.[2] Remarkably, heating this complex results in a thermally induced four-electron reduction at silicon, accompanied by the elimination of two equivalents of H_2, thereby generating the unprecedented silylene dianion $[SiH_2]^{2-}$, stabilised within the assembly. Notably, exposing this complex to an atmosphere of H_2 regenerates the hexahydridosilicate, establishing the first reversible Si(IV)/Si(0) redox cycle. Mechanistic studies and further reactivity will be discussed.

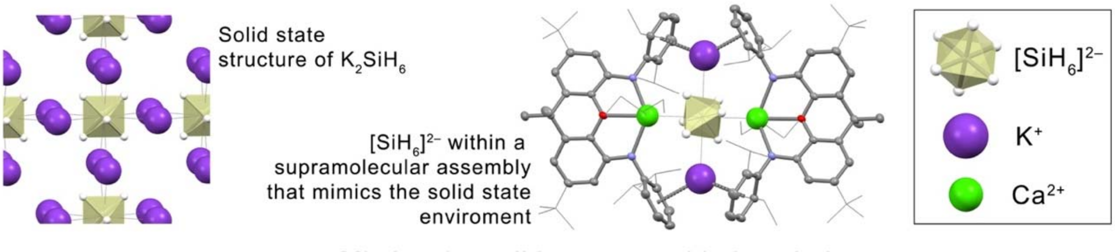

Figure 1. Representation of how the supramolecular assembly mimics the environment of the $[SiH_6]^{2-}$ anion in K_2SiH_6.[3]

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[1] J. S. McMullen, R. Huo, P. Vasko, A. J. Edwards, J. Hicks, *Angew. Chem. Int. Ed.* **2023**, e202215218.

[2] R. Huo, A. J. Armstrong, G. R. Nelmes, D. J. Lawes, A. J. Edwards, C. L. McMullin, J. Hicks, *Chem. Eur. J.*, **2024**, 30, *25*, e202400662.

[3] K. Puhakainen, D. Benson, J. Nylén, S. Konar, E. Stoyanov, K. Leinenweber, U. Häussermann, *Angew. Chem. Int. Ed.* **2012**, *51*, 3156-3160.