Solvation Experiments with Polysilicides in Liquid Ammonia


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Zintl ions are negatively charged, homo- or heteroatomic polyanions of the main group (semi-) metals,[1] These anions can be synthesized by solvolysis or by direct reduction of the metal by adding elemental alkali metal or alkaline earth metal in liquid ammonia or ethyldiamine.

However, for Silicon these polyanions are only known in binary or multinary solid state phases. In the case of molecular clusters, these contain tetrahedral [Si₄]⁺ and nine-atom [Si₉]⁺⁺ species with the ratio of 2:1 in A₁₁Si₁₂ (A = K – Cs) or only [Si₂]⁺⁺ ions in A₅Si₅ (A = Na – Cs).[2] Due to the poor solubility of the A₁₁Si₁₂ phases, A₅Si₅ serves as starting material for dissolution experiments, especially the mixed cation material K₄Rb₃Si₁₂. For these ionic and sensitive materials, liquid ammonia turned out to be the only suitable solvent. The solubility of the compounds can be improved by adding chelating agents like [18]crown-6 or [2.2.2]cryptand.

In this field, it is still uncertain what kind of solvation, transformation and crystallization processes of the materials take place during dissolution and recrystallization experiments. NMR spectroscopy proved to be the ideal method for characterizing the Zintl clusters in solution. This gives us the opportunity to improve the understanding of the solution chemistry of silicides, which is necessary to predict and control synthetic pathways.

### Experimental

- **Solvation Studies**: Studied the solvation processes in liquid ammonia to understand the solubility and stability of the Zintl clusters.
- **NMR Spectroscopy**: Used NMR spectroscopy to characterize the solvated anions and their transformations.
- **Simulation**: Performed computational simulations to predict the behavior of the clusters in solution.

### Results

- **Synthesis of [HSi₄]⁺⁻**: Represents the first protonated Si₄ cluster.
- **Hydrogen Atom Location**: The hydrogen atom could be located crystallographically.
- **Additional Signals**: Additionally, [²⁹Si⁻] (J(³⁵Si-H) = 22 Hz) and H-NMR spectra prove the presence of a hydrogen atom attached to the Si₄ cluster.

### Detection of [HSi₄]⁺⁻ by NMR Spectroscopy

- **Triplet Observation**: Two triplets at ~330 ppm and ~410 ppm may stem from the protonated silicic acid tetrahion [HSi₄]⁺⁻.
- **Cross-Peaks**: Additionally, two corresponding cross-peaks are detected in the ¹H – [²⁹Si] hMOC spectrum.
- **Theoretical Calculations**: Theoretical calculations indicate that two silicon atoms are bridged by one hydrogen atom.

### Synthesis of Complexes

- **K₉Rb₂[MesCu(η³-Si₂)] · 5NH₃**: First chelate-free crystal structure of a silicide transition metal complex containing the highly charged [Si₂][³⁻]
- **Rb₁₂K₂₈Si₂₇NH₃**: Homoleptic ammine complexes [K(NH₃)₆]⁻ (a), [K/Rb-Si₄] interactions are formed where the complexes (a) are located.[3]
- **Cs₉[SIP₃]**: The cesium phosphidosilicate Cs₉[SIP₃]³⁻, where silicon and phosphorus form isolated carbonate-like [SIP₃]⁺⁻ units, to a small extend dissolves in liquid ammonia.

### Outlook

Silicides represent interesting and promising building blocks, i.e. for the synthesis of new compounds containing transition metal complexes. These clusters are stable without organic substituents and facilitate rational reaction design due to their negative charge. However, our main focus lies on a better understanding of solvation, transformation and crystallization processes of the Zintl anions during dissolution and recrystallization.

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