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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 ethylenediamine.

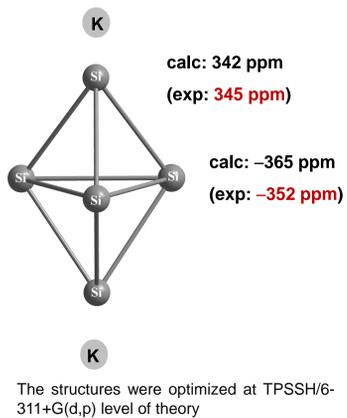
However, for Silicon these polyanions are only known in binary or multinary solid state phases. In the case of molecular clusters, these contain tetrahedral $[\text{Si}_4]^{4-}$ and nine-atom $[\text{Si}_9]^{3-}$ species with the ratio of 2:1 in $\text{A}_{12}\text{Si}_{17}$ (A = K – Cs) or only $[\text{Si}_4]^{4-}$ ions in A_4Si_4 (A = Na – Cs).^[2]

Due to the poor solubility of the A_4Si_4 phases, $\text{A}_{12}\text{Si}_{17}$ serves as starting material for dis-

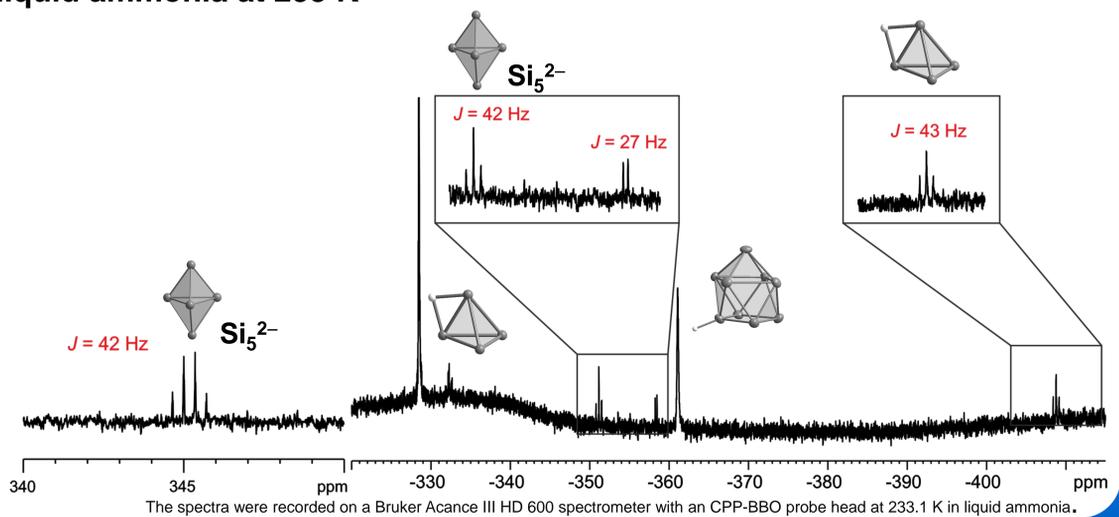
solution experiments, especially the mixed cation material $\text{K}_6\text{Rb}_6\text{Si}_{17}$. For these ionic and sensitive compounds, liquid ammonia turned out to be the only suitable solvent. The solubility of the compounds can be improved by adding chelating agents like [18]crown-6 or [2.2.2]cryptand.

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.

Computational simulation and experimental ^{29}Si spectra in liquid ammonia at 233 K

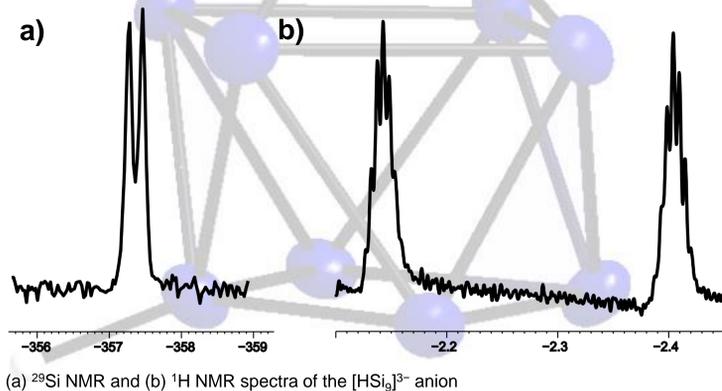


- For solvation experiments, [2.2.2]-cryptand was added to increase the solubility and to stabilize the solution.^[3]
- The extremely upfield shifted quadruplet at +345 ppm couples with a triplet at -352 ppm. The two signals pertain to the trigonal bipyramidal Si_5^{2-} .
- HMQC measurements indicate that the other signals stem from protonated silicide clusters



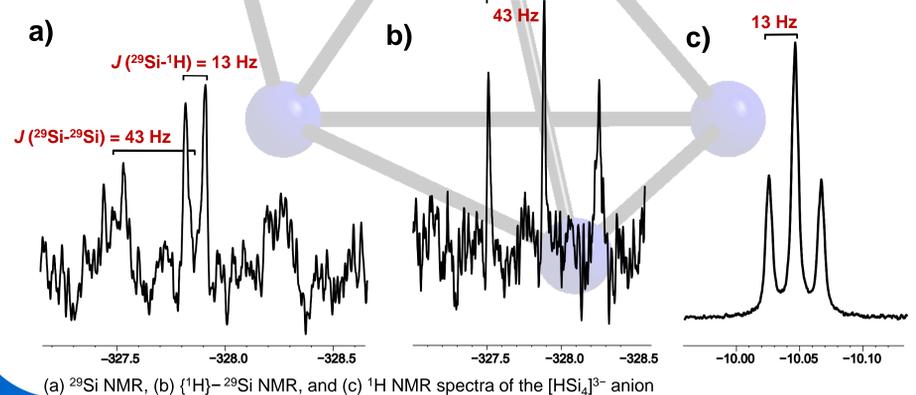
Synthesis of $[\text{HSi}_9]^{3-}$

- $[\text{HSi}_9]^{3-}$ represents the first protonated Si_9 cluster
- The hydrogen atom could be located crystallographically
- Additionally, ^{29}Si - ($^1J(^{29}\text{Si}-^1\text{H}) = 22 \text{ Hz}$) and ^1H -NMR spectra prove the presence of a hydrogen atom attached on the Si_9 cluster

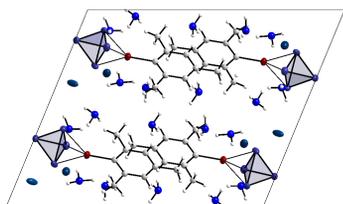


Detection of $[\text{HSi}_4]^{3-}$ by NMR Spectroscopy

- The two triplets at -330 ppm and -410 ppm may stem from the protonated tetrasilicide tetraanion $[\text{HSi}_4]^{3-}$.
- Additionally, two corresponding cross-peaks are detected in the $^1\text{H} - ^{29}\text{Si}$ HMQC spectrum
- Theoretical calculations and the reduced coupling constant $^1J(^{29}\text{Si}-^1\text{H}) = 13 \text{ Hz}$ indicate that two silicon atoms are bridged by one hydrogen atom.



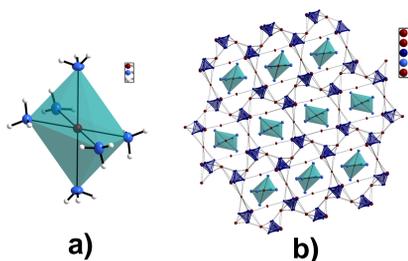
$\text{K}_2\text{Rb}_2[\text{MesCu}(\eta^3\text{-Si}_4)] \cdot 5\text{NH}_3$



- First chelate-free crystal structure of a silicide transition metal complex containing the highly charged $[\text{Si}_4]^{4-}$

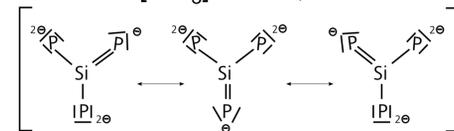
$\text{Rb}_{1.2}\text{K}_{2.8}\text{Si}_4 \cdot 7\text{NH}_3$

- Homoleptic ammine complexes $[\text{K}(\text{NH}_3)_6]^+$ (a)
- (b): K/Rb- Si_4 interactions tubes are formed where the complexes (a) are located.^[2]

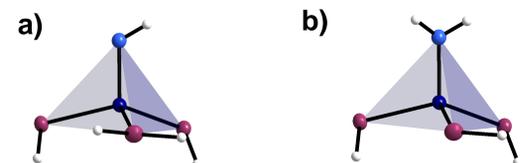


Dissolving $\text{Cs}_5[\text{SiP}_3]$

- The cesium phosphidosilicate $\text{Cs}_5[\text{SiP}_3]$ ^[4], where silicon and phosphorus form isolated carbonate-like $[\text{SiP}_3]^{5-}$ units, to a small extent dissolves in liquid ammonia



- After a few weeks, yellow crystals could be obtained. Despite of the high charge, the SiP_3 unit stays stable. The phosphorus atoms are protonated and an imido $[(\text{NH})\text{Si}(\text{PH}_2)(\text{PH})_2]^{3-}$ (a) / amido $[(\text{NH}_2)\text{Si}(\text{PH})_3]^{3-}$ (b) species is formed



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.

[1] S. Scharfe, F. Kraus, S. Stegmaier, A. Schier, T. Fässler, *Angew. Chem.*, **2011**, 123, 3712; *Angew. Chem. Int. Ed.*, **2011**, 50, 3630.

[2] C. Lorenz, S. Gärtner, N. Korber, *Z. Anorg. Allg. Chem.*, **2017**, 643, 141-145.

[3] M. Neumeier, F. Fendt, S. Gärtner, C. Koch, T. Gärtner, N. Korber, R. M. Gschwind, *Angew. Chem. Int. Ed.*, **2013**, 52, 4483-4486.

[4] B. Eisenmann, J. Klein, M. Somer, *Angew. Chem. Int. Ed.*, **1990**, 29, 87-88.