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Main-Group Chemistry

Detection of the Elusive Highly Charged Zintl Ions Si_4^{4-} and Sn_4^{4-} in Liquid Ammonia by NMR Spectroscopy

Maria Neumeier, Franziska Fendt, Stefanie Gärtner, Carina Koch, Tobias Gärtner, Nikolaus Korber, and Ruth M. Gschwind**

The appeal of Zintl anions originates from the fact that they are molecular building blocks of main-group elements that may be manipulated in solution. Apart from their intrinsic significance for the chemistry of the elements, they are promising starting materials for the development of new hybride materials containing transition metals and main-group elements.[1] The solution chemistry of the bare clusters also offers the possibility to find new elemental modifications by oxidative coupling, as was shown for germanium, or to create potential semiconducting amorphous or crystalline films by anodical deposition.[2,3] The dominant characterization method for nearly all of the reported compounds and materials has so far been single-crystal X-ray structure analysis. In contrast, much less is known about the species that actually occur in solution. To better understand the complicated processes which take place when Zintl anions react with reagents, the behavior of the bare polyanions in pure solutions must first be investigated. The long-range goal of these investigations would be a better understanding of Zintl anion solutions, thus facilitating an increasingly rational approach to their use in chemical transformations.

Solutions of Group 15 polyanions were studied intensely by Baudler et al.;[4] in contrast, a systematic investigation of ligand-free Group 14 polyanions in solution is still absent. Furthermore, highly reduced clusters, such as Sn_4^{4-} and Pb_4^{4-}, have never been detected in solution, and the observation of any silicides at all remains elusive. Therefore, our studies focused on the characterization of highly reduced homoatomic Group 14 polyanions in solution by using NMR spectroscopy. In previous ^{119}Sn NMR studies, Rudolph et al. reported the detection of Sn_9^{4-}. They documented a further upfield shifted signal, which was tentatively assigned to Sn_4^{2-}.[5–7] Moreover, Eichhorn et al. recently demonstrated the influence of [2.2.2]cryptand on Sn_9^{4-} species in solution. Their ^{119}Sn NMR studies showed that a stoichiometric excess (4.5 equivalents) of cryptand led to HSn_9^{3-} along with several different K^+-coordinated species $K_xSn_9^{(4-x)-}$ ($x = 0$–3).[8] More highly reduced clusters, such as Sn_4^{4-} and Pb_4^{4-}, have until now only been shown to exist in solution by the circumstantial evidence of solvate crystal structures, which were obtained from direct reduction experiments in liquid ammonia.[9] For the lighter homologues Si and Ge, the only known analoguous solvate crystal structure is a functionalized tetrahedral silicide.[10] An alternative route to access these E_4^{4-} clusters (E = Group 14 element) would be the dissolution of the precursor phases A_4E_4 (A = alkali metal), but they were presumed to be completely insoluble for the lighter congeners (E = Si, Ge, Sn).[1] Indeed, there has not been any report on an NMR signal of a bare homoatomic polyanion of silicon in solution to date. The only ^{29}Si signal for a negatively charged silicon cluster in solution stems from the $R_3Si_4^-$ anion, where $R = SiMe[CH(SiMe_3)_2]_2$, which was studied in toluene by Sekiguchi et al.[11] However, starting from the binary phases $A_{12}Si_{17}$ with one Si_9^{4-} and two Si_4^{4-} anions per formula unit (A = K, Rb), Sevov et al. were able to show that silicides may be dissolved in liquid ammonia to yield the oxidized polyanions Si_9^{3-}, Si_9^{2-}, and Si_5^{2-} in cryptand-containing solvate compounds.[12,13] In previous recrystallization experiments of a solid starting material with the nominal composition $K_6Rb_6Si_{17}$ in liquid ammonia, we were also able to indirectly find evidence for the existence of unoxidized Si_9^{4-} in solution,[14,15] and we also used this ternary material to form the complex ion $[\{Ni(CO)_2\}_2(\mu\text{-}Si_9)_2]^{8-}$.[16] Fässler et al. also succeeded in the synthesis of a functionalized silicide, $[(MesCu)_2(\eta^3\text{-}Si_4)]^{4-}$ (Mes = 2,4,6-$Me_3C_6H_2$), which contains Si_4 tetrahedra bonded to copper, in liquid ammonia from a similar starting material.[10] Considering these results, the question if and which silicide species may be detected in solution became urgent.

Herein we present the first NMR signal of a bare silicide in solution. To our knowledge, the detected Si_4^{4-} signal is the most upfield-shifted ^{29}Si signal of a tricoordinated Si atom in a molecular environment without the involvement of any transition-metal complex. Therefore, the upfield limit of the NMR scale of measured ^{29}Si signals is now extended from −274.2 ppm[17] to −323 ppm. Furthermore, we provide the first experimental evidence that Rb_4Sn_4 is soluble in liquid ammonia and that Sn_4^{4-} can be stabilized in solution in the presence of [2.2.2]cryptand. We also observe the oxidation of Sn_4^{4-} to Sn_9^{4-} in these solutions and, based on the detection of NH_2^-, unambiguously identify the oxidizing agent as being protons. This knowledge about solution processes of Group 14 polyanions might provide the possibility of rational syntheses of functionalized Zintl clusters and opens an approach to material design.

For the study of the highly charged Sn_4^{4-} and Si_4^{4-} clusters in solution, we selected the stannide system as a starting point.

[*] Dr. M. Neumeier, C. Koch, Dr. T. Gärtner, Prof. Dr. R. M. Gschwind
Institut für Organische Chemie, Universität Regensburg
93040 Regensburg (Germany)
E-mail: ruth.gschwind@ur.de
F. Fendt, Dr. S. Gärtner, Prof. Dr. N. Korber
Institut für Anorganische Chemie, Universität Regensburg
93040 Regensburg (Germany)
E-mail: nikolaus.korber@ur.de

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With respect to the detection of stannides, a convenient NMR approach has already been established, in which ^{119}Sn is observed and the ^{117}Sn satellite pattern is used for the assignment of the cluster sizes Sn_x (for details, see the Supporting Information).[5–8] Furthermore, stannides provide higher stability towards moisture and oxidation processes as well as better solubility than the highly sensitive silicides. For the synthesis, we chose the direct reduction of elemental tin with elemental rubidium (1:1) in liquid ammonia, because this additive-free preparation method minimizes external influences on the properties and the preferred cluster sizes and it allowed the crystallization of the solvates $A_4Sn_4{\cdot}2NH_3$ (A = Rb, Cs) in previous studies.[9]

With this setup, a small ^{119}Sn signal at −1727 ppm with a coupling constant of 1466 Hz and a ^{117}Sn satellite pattern of 0.13:1.00:0.12 was observed (Figure 1 a), despite the fact that the solubility of Sn_4^{4-} is expected to be very limited. In additive-free crystal structures, exclusively Sn_9^{4-} and Sn_4^{4-} have been observed;[1] for A_4Sn_9 clusters (A = alkali metals), the chemical shift range as well as the scalar coupling constants in ethylenediamine (en) are well-known (−1115–−1241 ppm; 256–293 Hz).[7] The upfield shift of the detected ^{119}Sn signal at −1727 ppm indicates a higher negative charge per Sn atom than Sn_9^{4-}, and the large coupling constant of 1466 Hz hints at a smaller cluster size. Both parameters and also the ^{117}Sn satellite pattern are in accordance with the assignment to Sn_4^{4-}, but owing to the limited signal-to-noise ratio (S/N) in the experiment with the sample prepared by direct reduction, slightly larger or smaller stannide clusters with five or three Sn atoms cannot be unambiguously excluded. Therefore, the solubility improving and stabilizing effect of [2.2.2]cryptand[18,19] was used for dissolution experiments on Rb_4Sn_4 in liquid ammonia. Prior to dissolution, solid Rb_4Sn_4 was characterized by Raman spectroscopy and X-ray diffraction (see the Supporting Information), which confirmed the presence of Sn_4^{4-} as the exclusive anionic moiety (Figure 1 b). Despite the fact that Rb_4Sn_4 has been assumed to be insoluble,[1] a broad signal covering 21 000 Hz appeared in the ^{119}Sn spectrum after 7.5 h of dissolution and 7.5 h of acquisition and sharpened within 4 days to a signal at −1825 ppm, which shows a surprisingly high S/N of 196 (Figure 1 c). This allowed the unambiguous assignment to Sn_4^{4-} by simulation of the experimental ^{117}Sn satellite pattern (0.133:1.000:0.132; see Figure 1 d) and shows a coupling constant (1423 Hz) that is similar to the direct reduction. The signal of Sn_4^{4-} in the presence of [2.2.2]cryptand is significantly shifted upfield compared to the additive-free direct reduction sample ($\Delta\delta = -98$ ppm). This is in agreement with previous reports about the effect of different counterions or [2.2.2]cryptand on the chemical shift of Sn_9^{4-}, where the degree of ion dissociation or sequestration correlates with upfield shifts.[7,8] The larger absolute upfield shift for Sn_4^{4-} compared to Sn_9^{4-} is in accordance with the higher negative charge per Sn atom. In contrast, in dissolution experiments on Rb_4Sn_4 without [2.2.2]cryptand, exclusively Sn_9^{4-} was detected (−1248 ppm, $J = 263$ Hz). Interestingly, the intensity of this signal grew over time and simultaneously the signal of NH_2^- appeared in the proton spectrum (see the Supporting Information). This is to our knowledge the first experimental evidence for the long standing suggestion that protons of ammonia or other solvents act as the oxidizing agent in the oxidation of Sn_4^{4-} to Sn_9^{4-}. Thus, direct reduction experiments of elemental tin with elemental rubidium (1:1) in combination with dissolution experiments of Rb_4Sn_4 with and without [2.2.2]cryptand not only allowed the first detection and the assignment of the highly charged cluster Sn_4^{4-} but also for the identification of ammonia as the potential oxidizing agent.

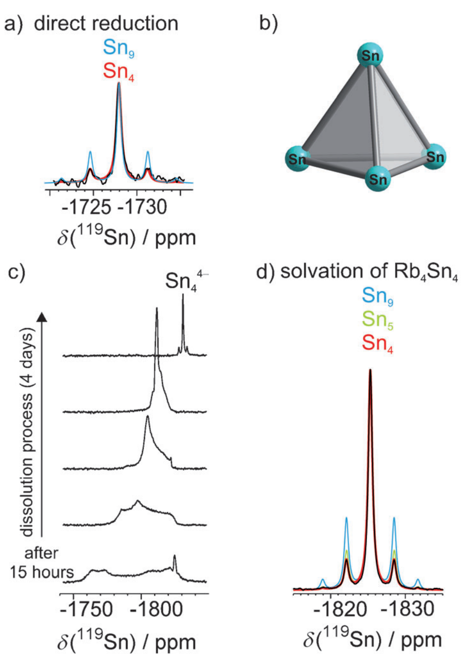

Figure 1. Sn_4^{4-} in liquid ammonia: a) experimental (black) and simulated (colored) ^{119}Sn spectra of Sn_4^{4-} (195 K, 224 MHz) resulting from direct reduction; b) Sn_4^{4-} cluster present in Rb_4Sn_4; c) ^{119}Sn spectra showing the dissolution process of Rb_4Sn_4 in the presence of [2.2.2]cryptand (233 K, 224 MHz); d) assignment to Sn_4^{4-} based on simulations of the ^{117}Sn satellite pattern.

Next, we focused on the detection of bare silicides in solution. To date, there is only circumstantial evidence for dissolved silicide clusters, but direct observation by ^{29}Si NMR has remained elusive. The only known NMR signals of silicides have been reported in solid-state MAS-NMR studies of the binary phases ASi (A = alkali metal). Progressing from Cs to Na, an upfield trend of the signals is observed, in accordance with a reduced electron transfer between cluster anion and counterion.[20,21] For Rb and K it was even possible to resolve the two crystallographic sites, which resulted in separated NMR signals for each phase (Rb −290, −305 ppm; K −320, −340 ppm). Given the tremendous intensity enhancement of Sn_4^{4-} in the dissolution experiments with [2.2.2]cryptand compared to the direct reduction, the cryptand-aided dissolution method was also chosen for the detection of silicides. Based on our experience with recrystallization experiments[14,15] and conversion[16] of silicides, a solid with the nominal composition $K_6Rb_6Si_{17}$ was used as the starting material. The $A_{12}Si_{17}$ phases (A = alkali metal) are the only silicides with known solubility. To facilitate the NMR detection in solution, ^{29}Si isotope labeling was applied. For

$K_6Rb_6Si_{17}$, an enrichment of 20% ^{29}Si was chosen as a compromise between absolute signal enhancement and intensity reduction owing to ^{29}Si–^{29}Si scalar couplings that would be expected for example for Si_9^{4-}. Prior to the solvation experiments, the characterization of the mixed cationic solid $K_6Rb_6Si_{17}$ by Raman spectroscopy showed the presence of both Si_4^{4-} and Si_9^{4-} clusters precast in the solid state (see Figure 2a and the Supporting Information). Deviating from that, the X-ray powder diffraction pattern showed only the presence of the binary Si_4^{4-}-containing phase Rb_4Si_4 (see the Supporting Information), which was attributed to the poor crystallinity and the plural phase character of the solid starting material. In the solid-state MAS-NMR of $K_6Rb_6Si_{17}$, only elemental Si and a broad signal at −311 ppm was observed (Figure 2b), which is exactly between the known chemical shifts of Rb_4Si_4 and K_4Si_4.[20,21] Again no signal for Si_9^{4-} was detected, which is probably due to line-broadening effects caused by scalar coupling and the poor crystallinity of the material, which also prohibited its detection in the X-ray powder diffraction pattern. Next, $K_6Rb_6Si_{17}$ was dissolved in the presence of cryptand in liquid ammonia, and the first ^{29}Si spectrum of the sample was started after 19 h. Unexpectedly, after 4.5 h of acquisition time and without further optimization of the NMR parameters, an extremely broad signal covering 180 Hz appeared in the ^{29}Si NMR spectrum, which sharpened within 11 days to a signal at −323 ppm with an extremely high signal to noise ratio of 80 (see Figure 2c and the Supporting Information). Therefore, this signal was assigned to a specific silicide cluster. ^{29}Si is the only NMR-active silicon isotope, and thus only the chemical shift can be used to differentiate between Si_4^{4-} and Si_9^{4-}, which are both present in the starting material. The ^{29}Si signal detected in solution has an only slightly upfield shift (−323 ppm) compared to the solid-state MAS-NMR signal of Si_4^{4-} in $K_6Rb_6Si_{17}$ at −311 ppm. For Si_9^{4-}, no MAS-NMR signal has been reported, and thus the exact chemical shift range is unknown. However, from the trends observed for the stannides, a lower charge per atom shifts the signal considerably downfield (Sn_4^{4-} −1727 ppm; Sn_9^{4-} −1248 ppm). Thus, the signal of Si_9^{4-} is expected to be in between the solid state signal of Si_4^{4-} and elemental Si. The chemical shift reported for $R_3Si_4^-$ in solution ($\delta = -153.6$ ppm; R = SiMe[CH(SiMe$_3$)$_2$]$_2$) corroborates this trend.[11] Furthermore, theoretical calculations suggest a higher rigidity for Si_9^{4-} than for Sn_9^{4-},[15] which would result in three separated signals for Si_9^{4-} (Figure 2a).

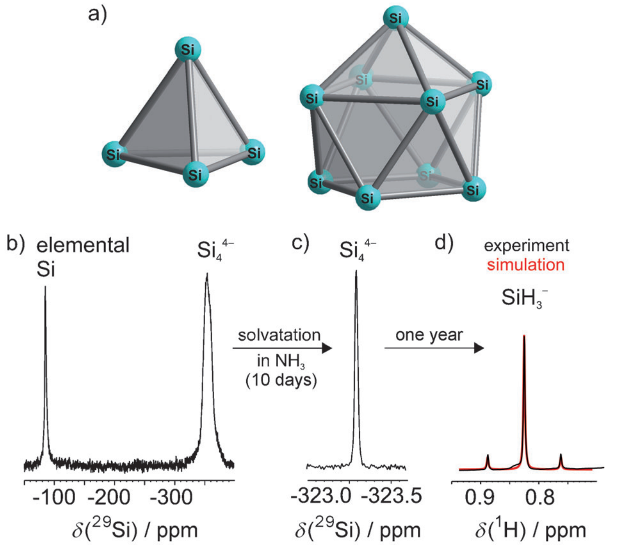

Figure 2. NMR detection of Si_4^{4-} in the solid state and in solution along with identification of the degradation product SiH_3^-: a) Si_4^{4-} and Si_9^{4-} clusters present in $K_6Rb_6Si_{17}$; b) ^{29}Si MAS-NMR spectrum of $K_6Rb_6Si_{17}$ with 20% ^{29}Si labeling at RT; c) ^{29}Si NMR spectrum after dissolution of the 20% ^{29}Si labeled $K_6Rb_6Si_{17}$ in the presence of [2.2.2]cryptand in liquid ammonia (195 K, 119 MHz); d) ^1H NMR spectrum (195 K, 600 MHz) after dissolution of the 20% ^{29}Si-labeled $K_6Rb_6Si_{17}$ without [2.2.2]cryptand in liquid NH_3 and one year storage at 195 K including the simulation (red) of SiH_3^-.

This fact and all of the chemical shift trends for known silicides and stannides corroborate the assignment to Si_4^{4-}. Next, the slight upfield shift between Si_4^{4-} in solution and in the MAS-NMR spectrum is addressed. As discussed above for stannides, the dissociation of cations from Zintl anions induces upfield shifts. For the highly charged Sn_4^{4-} signal without and with cryptand separating the cations from the clusters, an upfield shift of $\Delta\delta = -98$ ppm is observed (see above). For ^{29}Si, the absolute chemical shift range is significantly smaller. Thus, the upfield shift of Si_4^{4-} in solution by only 12 ppm with respect to the MAS-NMR signal fits to the ion sequestration during the dissolution process. Beyond that, Si_4^{4-} was observed to be surprisingly stable in the presence of [2.2.2]cryptand. Even in a sample of $K_6Rb_6Si_{17}$, which was stored at 195 K for one further month and measured at an elevated temperature of 233 K, the Si_4^{4-} signal was detected in 87% of the maximal intensity observed after 11 days at 195 K (see the Supporting Information). After an extended storage (one year) of $K_6Rb_6Si_{17}$ in liquid ammonia without [2.2.2]cryptand, a variety of degradation products was observed in the proton spectrum (see the Supporting Information). Among these, the signal at 0.83 ppm with a $^1J_{H,Si} = 75$ Hz could be identified as SiH_3^-. The simulation considering the 20% ^{29}Si labeling (Figure 2d) and the coupling constant of the previously reported signal of $KSiH_3$ in benzene[22] corroborate this assignment. Recently, Eichhorn et al. reported the protonated stannide HSn_9^{3-} in a reversible equilibrium with Sn_9^{4-} in the presence of [2.2.2]cryptand in ethylenediamine.[8] For the less stable silicides without the stabilizing influence of [2.2.2]cryptand, the protonation is expected to be irreversible, resulting in the formation of SiH_3^- as final degradation product.

In summary, the detection of silicides in solution, which has been elusive for a long time, has been achieved for Si_4^{4-}. Furthermore, the elusive first NMR observation of the highly charged stannide Sn_4^{4-} is reported. Amazingly high signal intensities and stabilities were observed for both highly charged Zintl anions, Si_4^{4-} and Sn_4^{4-}, by utilizing the stabilizing effect of [2.2.2]cryptand, and in the case of Si_4^{4-} the enhanced solubility of the mixed cationic starting material $K_6Rb_6Si_{17}$. Furthermore, by observing the generation of NH_2^-, the first experimental evidence for the longstanding assumption that solvent protons act as oxidizing agent on Zintl anions is given, and in case of silicides, SiH_3^- was detected as a degradation product.

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