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Aromaticity

Li NMR Spectroscopy on Crystalline $Li_{12}Si_7$: Experimental Evidence for the Aromaticity of the Planar Cyclopentadienyl-Analogous Si_5^{6-} Rings[**]

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Since the pioneering work of West et al. in 1981[1] that questioned the well-known double-bond rule, chemists working in the field of organometallics have been trying to synthesize silicon analogues of organic compounds containing π bonds. However, most of these compounds inherently lack thermodynamic stability, thus making their preparation a very challenging task. In these compounds, Si=Si π bonds have to be kinetically stabilized by large, sterically hindering groups. Very recently, Abersfelder et al.[2] reported the synthesis of a tricyclic isomer of hexasilabenzene containing a Si_6 ring. Theoretical calculations suggest a nonclassical “dismutational” aromaticity of the nonplanar hexasilabenzene.[3] However, classical benzene-like aromaticity is characterized by planarity and equal bond lengths that lead to an optimum overlap of the p orbitals to result in a cyclic electron delocalization. This effect increases the corresponding diamagnetic susceptibility.

Nuclear magnetic resonance (NMR) spectroscopy is a powerful technique that can be used to experimentally assess whether a structure should be regarded as aromatic or not. Aromatic compounds show characteristic and relatively large chemical shifts δ_{iso}, which are explained by a ring current induced by the magnetic field.[4] A probe nucleus residing inside the anisotropic cone above or below the aromatic ring will be subjected to a shielding effect (upfield shift) that causes the NMR signal to appear at lower δ_{iso} values. To the best of our knowledge, classical aromaticity characterized by the criteria mentioned above has not been reported to date for a structural unit solely composed of Si. Lee and Sekiguchi[5] previously reported two probably aromatic, positively charged complex ligands containing Si_3 and Si_4 rings. The Si_4 ligands are nearly planar and their formal charge agrees with the Hückel rule;[6] these features are a good argument for the aromaticity of these compounds. However, the ultimate proof of their (carbon-like) aromaticity is still missing.

In this work, the crystalline Zintl phase $Li_{12}Si_7$ was investigated by both 1D and 2D ^6Li as well as ^7Li high-resolution, that is, magic angle spinning (MAS) NMR spectroscopy. The crystal structure of the binary silicide contains semi-infinite 1D $^1_\infty[LiSi_{10/2}]$ sandwich complexes (Figure 1).[7] Remarkably, the corresponding Li MAS NMR spectrum exhibits a distinct signal that is shifted upfield to −17.2 ppm. As we will show here, there is strong evidence that this NMR signal belongs to the Li ions sandwiched between the cyclopentadienyl-analogous Si_5^{6-} rings in $Li_{12}Si_7$. The suspected aromaticity of the planar Si_5^{6-} units, see for example Ref. [7b,c], results in a pronounced shielding of these

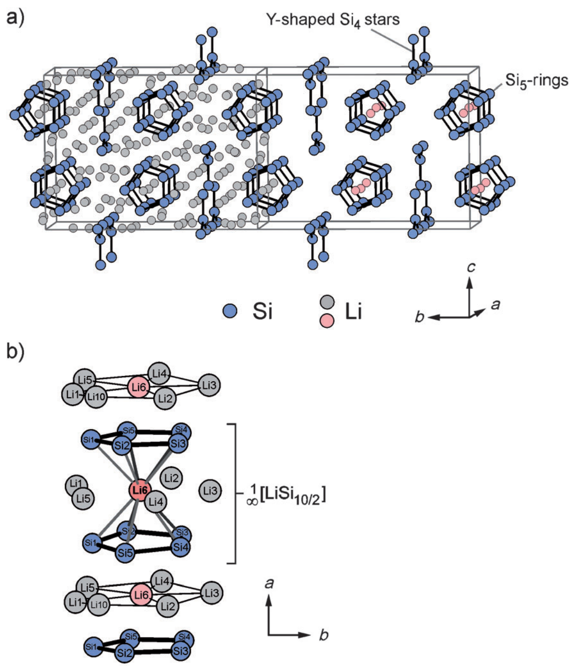

Figure 1. a) Crystal structure of the Zintl phase $Li_{12}Si_7$ (*Pnma*). In the right-hand unit cell, all Li atoms apart from Li6 are removed. b) Semi-infinite 1D sandwich complexes of $^1_\infty[LiSi_{10/2}]$ in $Li_{12}Si_7$. The notation follows that of Nesper et al., see Ref. [7b].

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Li ions. These rings, which are solely composed of silicon instead of carbon, meet the structural and magnetic criteria that are necessary for classical aromaticity.

Long before the work of West et al.,[1] a large variety of Si-containing Zintl phases that show all kinds of Si–Si bonding situations were reported (see, for example, Ref. [8]). In a simple picture, in Zintl-type silicides, the silicon substructure is "forced" to distribute the additional electrons obtained from the electropositive metal. This process leads to a variety of different bonding situations including the formation of π bonds. While Si=Si π bonds in organometallic molecular compounds need to be kinetically stabilized and protected from electrophilic attack by large sterically hindering groups, Si=Si π bonds in Zintl-phase compounds are stabilized because of the mere absence of any electrophilic atom or group. Therefore, these compounds are not only kinetically stabilized but thermodynamically stable as long as the pure compound is considered.

Planar silicon rings[7a,9] can be found in some of these phases. In particular, this is the case for the (nonparamagnetic) Zintl-type binary silicide $\mathrm{Li_{12}Si_7}$ containing linear semi-infinite chains of $^{1}_{\infty}[\mathrm{LiSi_{10/2}}]$ sandwich complexes (Figure 1.[10] It is noteworthy that the latter structural motif is also present in the ternary compound $\mathrm{Li_8MgSi_6}$[9] (see the Supporting Information). The unit cell of the Zintl phase $\mathrm{Li_{12}Si_7}$ is best described as $(\mathrm{Li_6}^{6+}[\mathrm{Si_5}]^{6-})_2\ (\mathrm{Li_{12}}^{10+}[\mathrm{Si_4}]^{10-})_2$ and gives rise to two distinct arrangements of Si atoms, that is, planar $\mathrm{Si_5}$ rings and 'Y'-shaped $\mathrm{Si_4}$ stars (see Figure 1). This structural model (Zintl ion concept) attributes the 26 electrons (20 Si + 6 Li) to the $\mathrm{Si_5}^{6-}$ ring, thus satisfying Hückel aromaticity.[6] Theoretical studies predicted the aromaticity of the $\mathrm{Si_5}^{6-}$ ring (see Ref. [10] and references therein), however, this aromaticity has not been experimentally proven to date.

The Li NMR spectra shown here were recorded on a highly pure, polycrystalline $\mathrm{Li_{12}Si_7}$ (natural abundance, 92.5 % ^{7}Li, 7.5 % ^{6}Li), which was prepared under Ar atmosphere in a niobium ampoule (for experimental details see the Supporting Information). The product was characterized by X-ray powder diffraction, and shows orthorhombic symmetry (*Pnma*). The refined lattice parameters are $a = 860.3(2)$, $b = 1976.9(4)$, $c = 1434.9(4)$ pm. These values are in very good agreement with the reported values. Variable-temperature Li MAS NMR spectra were recorded using a Bruker Avance III spectrometer in combination with a commercial 2.5 mm MAS probe (Bruker BioSpin). The spectrometer is connected to a cryomagnet with a shimmed magnetic field B_0 of 14.1 T. NMR spectra were recorded at a spinning frequency of 30 kHz.

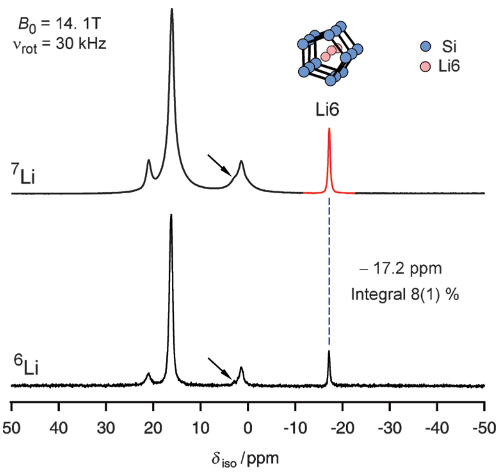

Figure 2. 1D ^{7}Li and ^{6}Li MAS NMR spectra of $\mathrm{Li_{12}Si_7}$ at room temperature (bearing gas temperature) recorded at an external magnetic field B_0 of 14.1 T and a spinning frequency ν_{rot} of 30 kHz. The integral under the NMR signal at −17.2 ppm amounts to 8(1) % of the total integral of the spectrum. The arrow denotes a minor decomposition phase arising from unavoidable air contact in the MAS rotor.

^{7}Li and ^{6}Li MAS NMR spectra of $\mathrm{Li_{12}Si_7}$ measured at room temperature (bearing gas temperature) are composed of four clearly resolved signals (Figure 2). Not all the crystallographic sites are resolved at room temperature because of extremely fast exchange processes of the Li ions residing outside the chains[11] shown in Figure 1. In particular, the ^{7}Li MAS NMR spectra recorded at temperatures as low as 140 K (not shown here for the sake of brevity) show that the signal with the highest intensity (see Figure 2) is a coalesced signal with a mean chemical shift of $\delta = 16.1$ ppm at room temperature. As mentioned above, the Li NMR spectra show a clearly recognizable signal at $\delta_{iso} = -17.2$ ppm, which is independent of temperature (140–335 K). In general, the chemical shifts of $\mathrm{Li^+}$ ions in nonparamagnetic and nonmetallic compounds are very small (i.e., well below ± 10 ppm; see, for example, Ref. [12]). In our opinion, the existence of a ring current in the cyclopentadienyl-like $\mathrm{Si_5}^{6-}$ units in $\mathrm{Li_{12}Si_7}$, which are isoelectronic with $\mathrm{P_5}^-$,[13] is the simplest explanation for an upfield shift as large as −17.2 ppm. This explanation is in good agreement with previous considerations of Nesper, von Schnering, and Curda[7b] (see also Ref. [7c]). Indeed, the reported calculated values are in the same range as investigated here: the calculated so-called nucleus-independent chemical shift NICS(1)[14] of isoelectronic $\mathrm{P_5}^-$ amounts to values between −16 and −18 ppm depending on the procedure for calculating applied; the $\mathrm{NICS}_{zz}(1)$ value is reported to be −39.2 ppm.[15] The corresponding $\mathrm{NICS}_{zz}(1)$ value of $\mathrm{Si_5H_5}^-$ (−32.1 ppm) is similar to that of Cp^- (−33.7 ppm; Cp = cyclopentadienyl) while the calculated diamagnetic shielding in slightly distorted (nonplanar) $\mathrm{Si_5H_5}^-$ was much smaller (−19.3 ppm).[16] Based on these results, we conclude that the chemical shift of −17.2 ppm found in $\mathrm{Li_{12}Si_7}$ is largely due to an aromatic ring current.[17] Thus, the signal has to be identified with that of Li6 (see Figure 1 b), representing the Li site between the $\mathrm{Si_5}^{6-}$ rings. For comparison, the experimental value δ_{iso} of ^{6}Li in $\mathrm{LiCp_2}^-$ amounts to −13.1 ppm.[18] This assignment is further corroborated by the fact that the integral under the corresponding NMR line amounts to 8(1) %, which is in excellent agreement with the expected value of 8.3 % determined from the crystal structure. The same explanation is valid for the similarity of the corresponding Li NMR spectrum of ternary $\mathrm{Li_8MgSi_6}$[9] to that of $\mathrm{Li_{12}Si_7}$ (see the Supporting Information).

Finally, in order to exclude that the signal observed at $\delta_{iso} = -17.2$ ppm belongs to a second phase that is possibly present, 2D exchange Li MAS NMR experiments were carried out. The room-temperature ^{7}Li NMR spectra as well as ^{6}Li exchange NMR spectra of $\mathrm{Li_{12}Si_7}$, which were recorded at mixing times of 100 ms (^{7}Li) and 1 s (^{6}Li), respectively, are shown in Figure 3. Off-diagonal intensities clearly indicate slow chemical exchange between all of the peaks visible in the NMR spectrum. Cross-peaks are either caused by spin diffusion or translational jumps of the Li ions from one crystallographic site to another. Irrespective of their nature, their appearance unequivocally proves that the Li sites involved belong to the same structure. If the NMR signal at −17.2 ppm belonged to a separate phase, as recently assumed by the NMR study of Key et al.,[19] no off-diagonal intensities would be expected.

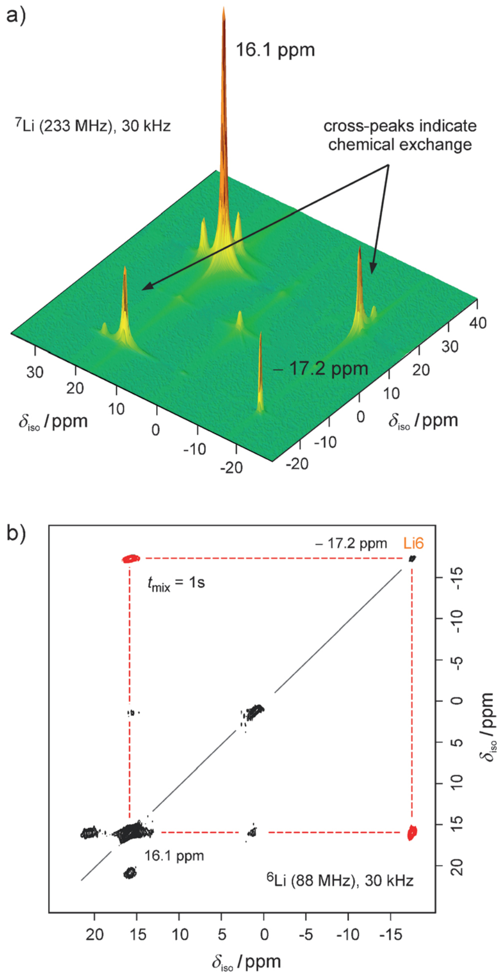

Figure 3. a) ^{7}Li 2D exchange MAS NMR spectrum of $Li_{12}Si_7$ at room temperature (bearing gas temperature) recorded at a magnetic field of 14.1 T and a spinning rate of 30 kHz using a mixing time of $t_m = 100$ ms. b) ^{6}Li 2D exchange MAS NMR spectrum recorded under the same conditions. The mixing time was 1 s. Dashed lines highlight the Li exchange between the signals showing up at 16.1 and −17.2 ppm. The corresponding off-diagonal intensities are shown in red.

A comparison of results from ^{7}Li with those from ^{6}Li 2D NMR shows that the cross-peaks detected are mainly due to Li jump processes rather than spin diffusion. The latter process is largely suppressed in the case of ^{6}Li 2D NMR because of the spatial separation of the ^{6}Li nuclei leading to a reduction of homonuclear dipole–dipole interactions. This enables the estimation of the Li exchange rate from mixing-time-dependent 2D NMR spectra. Here, as expected, the exchange rate associated with the signals that appear at −17.2 ppm and 16.1 ppm (see Figure 3 a) turns out to be rather low and amounts to be 70(5) s^{-1}. Obviously, the Li6 ions are locked by multiple interactions with the Si5 rings to result in such a small jump rate.

In conclusion, the Li MAS NMR spectrum of the Zintl phase $Li_{12}Si_7$ shows a distinct signal at −17.2 ppm. Usually, such a large upfield shift serves as a criterion for aromaticity. Indeed, the NMR signal can be unambiguously assigned to the Li6 ions located between the cyclopentadienyl-like Si_5^{6-} rings. These units are characterized by the typical structural and magnetic features of classical aromaticity known for carbon compounds, namely planarity, (nearly) equal bond lengths, and overlap between the p orbitals perpendicular to the Si_5^{6-} ring. Thus, the chemical shift observed experimentally confirms earlier studies that predict classical Hückel aromaticity of these rings that are composed solely of silicon instead of carbon.

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[1] R. West, M. J. Fink, J. Michl, *Science* **1981**, *214*, 1343.
[2] K. Abersfelder, A. J. P. White, H. S. Rzepa, D. Scheschkewitz, *Science* **2010**, *327*, 564.
[3] R. J. F. Berger, H. S. Rzepa, D. Scheschkewitz, *Angew. Chem.* **2010**, *122*, 10203; *Angew. Chem. Int. Ed.* **2010**, *49*, 10006.
[4] a) P. Lazzeretti, *Prog. Nucl. Magn. Reson. Spectrosc.* **2000**, *36*, 1; b) J. A. N. F. Gomes, R. B. Mallion, *Chem. Rev.* **2001**, *101*, 1349.
[5] V. Y. Lee, A. Sekiguchi, *Angew. Chem.* **2007**, *119*, 6716; *Angew. Chem. Int. Ed.* **2007**, *46*, 6596.
[6] W. v. E. Doering, F. L. Detert, *J. Am. Chem. Soc.* **1951**, *73*, 876.
[7] a) H. G. von Schnering, R. Nesper, J. Curda, K. F. Tebbe, *Angew. Chem.* **1980**, *92*, 1070; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 1033; b) R. Nesper, H. G. von Schnering, J. Curda, *Chem. Ber.* **1986**, *119*, 3576; c) W. Tiznado, N. Perez-Peralta, R. Islas, A. Toro-Labbe, J. M. Ugalde, G. Merino, *J. Am. Chem. Soc.* **2009**, *131*, 9426.
[8] a) R. Nesper, *Prog. Solid State Chem.* **1990**, *20*, 1; b) H. Axel, H. Schäfer, A. Weiss, *Angew. Chem.* **1965**, *77*, 379; *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 358.
[9] R. Nesper, J. Curda, H. G. von Schnering, *J. Solid State Chem.* **1986**, *62*, 199.
[10] V. L. Chevrier, J. W. Zwanziger, J. R. Dahn, *J. Alloys Compd.* **2010**, *496*, 25.
[11] A. Kuhn, P. Sreeraj, R. Pöttgen, H.-D. Wiemhöfer, M. Wilkening, P. Heitjans, *J. Am. Chem. Soc.* **2011**, *133*, 11018.
[12] H. Günther in *Encyclopedia of Nuclear Magnetic Resonance, Vol. 5* (Eds.: D. M. Grant, R. K. Harris), Wiley, Chichester, **1996**, p. 2807.
[13] E. Urnezius, W. W. Brennessel, J. C. Cramer, J. E. Ellis, P. von R. Schleyer, *Science* **2002**, *295*, 832.
[14] P. von R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317.
[15] J. O. C. Jiménez-Halla, E. Matito, J. Robles, M. Solà, *J. Organomet. Chem.* **2006**, *691*, 4359.

[16] A. P. Sergeeva, A. I. Boldyrev, *Organometallics* **2010**, *29*, 3951.

[17] Most recently, we have also found large NMR upfield shifts (up to −35 ppm) in the nonparamagnetic Zintl phases Li_7Si_3 and $Li_{13}Si_4$ containing Si_2 dumbbell units. The signals appear at low temperatures only and with low intensity. It is most likely that some of the Li ions form π complexes with the Si_2 dumbbells to result in a pronounced upfield shift. The preliminary NMR results point to a much more complex structure of these Zintl phases than those reported to date. It is worth mentioning that the corresponding shifts are absent for $Li_{21}Si_5$ containing isolated Si only.

[18] L. A. Paquette, W. Bauer, M. R. Sivik, M. Bühl, M. Feigel, P. von R. Schleyer, *J. Am. Chem. Soc.* **1990**, *112*, 8776.

[19] B. Key, R. Bhattacharyya, M. Morcrette, V. Seznéc, J.-M. Tarascon, C. P. Grey, *J. Am. Chem. Soc.* **2009**, *131*, 9239.