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$[Ge{=}Ge]^{4-}$ Dumbbells in the Zintl Phase Li_3NaGe_2

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When I started studying chemistry in the early 1980's, one of the very first rules I learned was that double bonds between third-row elements and their heavier homologues are not possible, since owing to the large size of these atoms, only a very weak overlap of the p orbitals occurs, which leads to unstable π bonding. In one of the very first textbooks on inorganic chemistry I bought as a freshman, you will find (in German): "*Doppel- und Dreifachbindungen kommen in Verbindungen erster Ordnung ganz allgemein nur bei Atomen mit kleinem Radius, also fast ausschließlich bei Elementen der ersten Achterperiode, nicht dagegen bei höheren Elementen mit größeren Atomradius vor ("Doppelbindungsregel").*" And: "*In der zweiten Achterperiode sind nur die kleinsten Atome (speziell die des Schwefels, weniger ausgeprägt die des Phosphors und Chlors) begrenzt zur Ausbildung von p_π-p_π-Bindungen befähigt.*"[1] It was almost the same year (1981) that West et al. synthesized the stable disilene $Mes_2Si{=}SiMes_2$ (Mes = mesityl or 2,4,6-trimethylphenyl).[2] In the following years, three separate X-ray crystal structures clearly showed that a Si=Si double bond must be assumed for this compound.[3] Since then, chemists have been able to synthesize numerous molecules with multiple bonds of Ga, Si, Ge, Sn, Pb and others.[4] Up to 1999, 10 R_2GeGeR_2 compounds had been published with potential Ge=Ge double bonds.[4a] Some of them are presented in Figure 1. The principle for synthesizing such compounds sounds simple: bulky substituents are introduced to shield and stabilize the reactive E=E/E≡E bonds.

Now let us consider a very simple—at least for solid-state chemists—experiment: take the elements lithium, sodium, and germanium and heat them under inert conditions to 750 °C. Single-crystal X-ray structure analysis of the resulting red, lustrous, air- and moisture-sensitive crystals reveals that Ge_2 dumbbells have been formed (Figure 2). By applying the Zintl–Klemm concept, that is, electrons of the electropositive elements lithium and sodium are transferred to the more electronegative germanium, the electron distribution of this compound is $(Li^+)_3(Na^+)(Ge_2^{4-})$. Ge_2^{4-} dumbbells are thus calculated, which should contain a Ge=Ge double bond without any bulky substituents. This would be indeed a spectacular result!

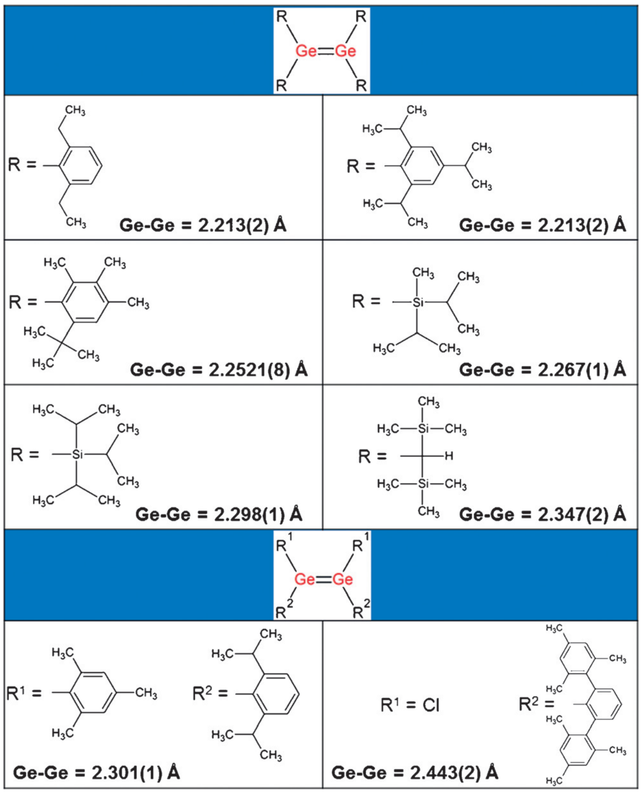

Figure 1. Selected molecules with Ge=Ge double bonds.[4a]

But how can we be sure that Ge=Ge double bonds have really been formed in Li_3NaGe_2? Isn't the Zintl–Klemm concept too simple as a reliable confirmation? In their recent publication, Fässler and co-workers, who conducted the synthesis of Li_3NaGe_2, present several complementary methods to corroborate their findings.[5] The simplest approach is probably a close look at the Ge=Ge bond length. For carbon, this approach is very straightforward: 1.54 Å points to C–C single bonds, 1.33 Å to C=C double bonds, and 1.20 Å typically to C≡C triple bonds. However, the story is not so simple for germanium. In Figure 1, the respective Ge=Ge bond lengths are given for each compound. They range from 2.21 to 2.44 Å, depending on the steric repulsion of the bulky substituents. For Li_3NaGe_2, a Ge=Ge bond length of 2.390(1) Å was determined. However, since in this case a "naked" Ge_2 dumbbell without any substituents and with a high charge on both Ge atoms exists, it should be better compared to

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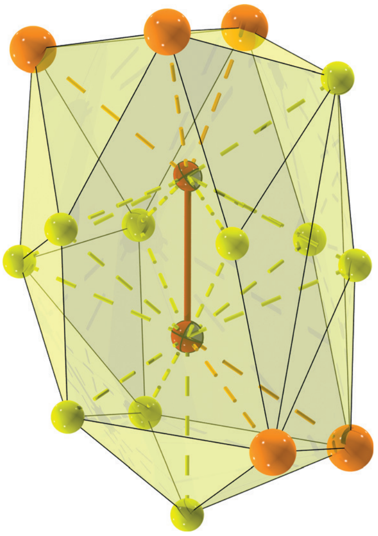

Figure 2. Coordination sphere of a Ge_2 dumbbell in the crystal structure of Li_3NaGe_2 (Ge red, 90% probability; Na orange; Li yellow).

other Ge_2 dumbbells in intermetallic compounds. For $BaMg_2Ge_2$, the Zintl–Klemm concept leads to $(Ba^{2+})(Mg^{2+})_2(Ge_2^{6-})$. A dumbbell with a Ge–Ge single bond is thus expected and accordingly a longer Ge–Ge bond length of 2.58 Å is found.[6] Similar results are obtained for some binary lithium germanides, for example, Li_9Ge_4, which can be written as $(Li^+)_9(Ge_2^{4.5-})_2$ according to the Zintl–Klemm concept. In Li_9Ge_4, $Ge{=}Ge^{4-}$ units with 0.5 excess electrons per dumbbell are found. This lead to a Ge–Ge bond length of 2.44 Å,[7] which is, as expected, somewhat longer than the respective bond length in Li_3NaGe_2.

However, bond lengths have sometimes been misleading, for example, in acetylides, since thermally induced disorder of the C_2 dumbbells around their centers of gravity may result in a decreased C–C bond length in the structural analysis.[8] Fässler and co-workers circumvented this problem by recording their single-crystal X-ray data at a temperature as low as 123 K.[5] The resulting ORTEP plot (Figure 2, only shown for the Ge atoms) does not give any hint on such a motion of the Ge_2 dumbbell, so the resulting Ge–Ge distance can be taken as very reliable.

You may find examples in the field of C_2 dumbbells containing carbides, which show that a simple correlation between bond length and bond order is sometimes hampered by the moderate quality of the determined C–C distances. For example, for CaC_2, according to $(Ca^{2+})(C_2^{2-})$ with a C–C triple bond, the expected bond length of 1.191(9) Å is found.[9] This bond is elongated to 1.28 Å in $LaC_2 \equiv (La^{3+})(C_2^{3-})$, since after the bonding states are filled, an excess electron occupies antibonding states in each $[C{\equiv}C]^{2-}$ unit.[10] In $La_2C_3 \equiv (La^{3+})_4(C_2^{4-})_3$, two excess electrons occupy antibonding states in each C_2 dumbbell, which should lead to a further increase of the C–C bond length. However, the C–C distances in $La_4(C_2)_3$, as determined by different authors, are wide-spread and range from 1.236 Å to 1.32 Å.[10,11] These imprecise results do not allow a simple correlation between bond length and bond order. To further corroborate their findings, Fässler at al. performed a thorough electronic structure calculation of Li_3NaGe_2 (TB-LMTO-ASA), which clearly indicated that π-antibonding Ge(p) states are occupied at the Fermi level. The resulting −iCOHP value of these states, which is an indicator for the bond strength in such band-structure calculations, is significantly larger (3.27 eV per Ge–Ge bond) than the respective values calculated for the Ge_2 dumbbells in M_7Ge_6 (M = Ca, Sr, Ba), with 2.48 to 2.92 eV per Ge–Ge bond,[12] thus again indicating that a strong Ge–Ge double bond is formed in Li_3NaGe_2.

Raman spectroscopy has been shown to be a versatile probe for characterisation of the bond order of C–C bonds, since the symmetric C–C stretching vibration is very sensitive to its electronic structure.[8,13] For acetylides with C–C triple bonds, wavenumbers for these vibrations ranging from $\tilde{\nu} = 1796\,\text{cm}^{-1}$ to $1998\,\text{cm}^{-1}$ have been reported.[13] For C–C double bonds, this signal is shifted to $\tilde{\nu} = 1700\text{-}1500\,\text{cm}^{-1}$, and for C–C single bonds a significant shift to even smaller wavenumbers is found. For Ge–Ge bonds, the signal for the symmetric stretching vibration is shifted to very small wavenumbers owing to the higher atomic weight of germanium. Fässler et al. report a $\tilde{\nu} = 230\,\text{cm}^{-1}$ band for the Ge–Ge stretching vibration. This is in the range found for other germanium Zintl anions, for example, $[Ge_9]^{4-}$ ($\tilde{\nu} = 220$–$222\,\text{cm}^{-1}$) and $[Ge_4]^{4-}$ ($\tilde{\nu} = 274\,\text{cm}^{-1}$).[14] But unfortunately, no spectra for other Ge_2 dumbbell containing compounds could be given for comparison. As is obvious from Figure 2, the coordination environment of the Ge_2 dumbbell is not symmetrical in Li_3NaGe_2, so the Ge–Ge stretching vibration should also be IR active. But IR spectra have not been reported to date.

Finally ^6Li and ^{23}Na solid-state MAS NMR data (MAS = magic angle spinning) were used as an indirect probe of the π-bonding character of the Ge_2 dumbbells. Li(1) and Li(3), which are surrounded in a trigonal planar arrangement by three side-on coordinating Ge_2 dumbbells, show an upfield NMR shift of $\delta = -10.0$ ppm. A similar ^6Li shift was found in Li cyclopentadienide ($\delta = -7.6$ ppm).[15]

To summarize Fässler et al. give convincing evidence that the Zintl compound Li_3NaGe_2 contains Ge_2^{4-} dumbbells with a Ge–Ge double bond. To date, there is no clear evidence for a solid with an analogous $[Si{=}Si]^{4-}$ dumbbell.[16] Most importantly, the Ge_2 dumbbell in Li_3NaGe_2 is not bound to any substituents, which leads to several interesting consequences. For the molecules given in Figure 1 a *trans*-bent structure is found, that is, the coordination around germanium is no longer planar like in the sp^2-hybridized carbon atom of, for example, ethene (C_2H_4). The unsubstituted Ge_2^{4-} dumbbell in Li_3NaGe_2, however, can be understood as an analogue of molecular oxygen (O_2) or Se_2 in the gas phase. The respective MO diagrams for O_2 and hypothetical Ge_2^{4-} in a vacuum are quite similar, so isolated Ge_2^{4-} should also be paramagnetic like O_2, since in both dimers, a single occupation of degenerate antibonding π* orbitals occurs.[5] In Li_3NaGe_2, however the Ge_2^{4-} dumbbells are embedded in a solid with metallic properties, which leads to diamagnetism, since the diamagnetic contributions of the ions overcompensate the expected Pauli paramagnetism of the conduction electrons. However, since it has been shown that Zintl compounds[17] as well as acetylides[18] can be dissolved in liquid ammonia, a solution of Li_3NaGe_2 in liquid ammonia should show paramagnetism. This might be an interesting goal for further research in this field, but it will definitely be difficult to stabilize such highly charged anions in solution. Other interesting prospects are syntheses of solids with $[E{=}E]^{4-}$ dumbbells of the homologues of germanium ($E = Si$, Sn, Pb). And finally, the synthesis of a compound with a $[E{\equiv}E]^{2-}$ dumbbell ($E = Si$–Pb) analogous to the acetylide anion (C_2^{2-}) seems to be another ambitious aim. As Fässler and co-workers have shown, Zintl phases could be a key to open the door to such compounds.

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[1] "In general, double and triple bonds are only known for compounds of atoms with small radii, that is, elements of the second period and not for elements of the third and higher periods with larger atomic radii ("double bond rule")." And: "In the third period, only the smallest atoms (especially sulfur and to a lesser degree phosphorous and chlorine) are to a limited extent able to form p_π–p_π bonds." (Translated by the author) from: Holleman-Wiberg, *Lehrbuch der Anorganischen Chemie*, 81.-90. ed., de Gruyter, Berlin, **1976**, p. 124.
[2] R. West, M. J. Fink, J. Michl, *Science* **1981**, *214*, 1343–1344.
[3] a) M. J. Fink, M. J. Michalczyk, K. Haller, R. West, J. Michl, *Organometallics* **1984**, *3*, 793–800; b) B. D. Shepherd, C. F. Campana, R. West, *Heteroat. Chem.* **1990**, *1*, 1–7; c) M. Wind, D. R. Powell, R. West, *Organometallics* **1996**, *15*, 5772–5773.
[4] a) P. P. Power, *Chem. Rev.* **1999**, *99*, 3463–3503; b) Y. Wang, G. H. Robinson, *Chem. Commun.* **2009**, 5201–5213.
[5] L. M. Scherf, A. J. Karttunen, O. Pecher, P. C. M. M. Magusin, C. P. Grey, T. F. Fässler, *Angew. Chem. Int. Ed.* **2016**, *55*, 1075–1079; *Angew. Chem.* **2016**, *128*, 1087–1091.
[6] a) B. Eisenmann, N. May, W. Müller, H. Schäfer, A. Weiss, J. Winter, G. Ziegleder, *Z. Naturforsch. B* **1970**, *25*, 1350–1352; b) B. Eisenmann, H. Schäfer, *Z. Anorg. Allg. Chem.* **1974**, *403*, 163–172.
[7] A. Grüttner, R. Nesper, H. G. von Schnering, *Acta Crystallogr. Sect. A* **1981**, *37*, C161.
[8] U. Ruschewitz, *Coord. Chem. Rev.* **2003**, *244*, 115–136.
[9] M. Atoji, *J. Chem. Phys.* **1961**, *35*, 1950–1960.
[10] M. Atoji, K. Gschneidner, Jr., A. H. Daane, R. E. Rundle, F. H. Spedding, *J. Am. Chem. Soc.* **1958**, *80*, 1804–1808.
[11] a) M. Atoji, D. Williams, *J. Chem. Phys.* **1961**, *35*, 1960; b) A. Simon, T. Gulden, *Z. Anorg. Allg. Chem.* **2004**, *630*, 2191–2198.
[12] L. Siggelkow, V. Hlukhyy, T. F. Fässler, *J. Solid State Chem.* **2012**, *191*, 76–89.
[13] U. Ruschewitz, *Z. Anorg. Allg. Chem.* **2006**, *632*, 705–719.
[14] a) W. Carrillo-Cabrera, R. Cardoso Gil, M. Somer, Ö. Persil, H. G. von Schnering, *Z. Anorg. Allg. Chem.* **2003**, *629*, 601–608; b) H. G. von Schnering, M. Baitinger, U. Bolle, W. Carrillo-Cabrera, J. Curda, Y. Grin, F. Heinemann, J. Llanos, K. Peters, A. Schmeding, M. Somer, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1037–1039.
[15] L. A. Paquette, W. Bauer, M. R. Sivik, M. Buehl, M. Feigel, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1990**, *112*, 8776–8789.
[16] H. Takayuki, H. Yamane, N. Becker, R. Dronskowski, *J. Solid State Chem.* **2015**, *230*, 390–396.
[17] a) K. Wiesler, K. Brandl, A. Fleischmann, N. Korber, *Z. Anorg. Allg. Chem.* **2009**, *635*, 508–512; b) M. Reil, N. Korber, *Z. Anorg. Allg. Chem.* **2007**, *633*, 1599–1602.
[18] M. Hamberger, S. Liebig, U. Friedrich, N. Korber, U. Ruschewitz, *Angew. Chem. Int. Ed.* **2012**, *51*, 13006–13010; *Angew. Chem.* **2012**, *124*, 13181–13185.

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