**Zintl Anions**

Deutsche Ausgabe: DOI: 10.1002/ange.201602837
Internationale Ausgabe: DOI: 10.1002/anie.201602837

# Cluster Fusion: Face-Fused Nine-Atom Deltahedral Clusters in $[Sn_{14}Ni(CO)]^{4-}$

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***Abstract:** The title anion was synthesized by heating dimethylformamide (DMF) solution of the known Ni-centered and Ni(CO)-capped tin clusters $[Ni@Sn_9Ni(CO)]^{3-}$. The new anion represents the first example of face-fused nine-atom molecular clusters. The two clusters are identical elongated tricapped trigonal prisms of nido-$[Sn_8Ni(CO)]^{6-}$ with nickel at one of the capping positions. They are fused along a triangular face adjacent to a trigonal prismatic base and made of two Sn and one Ni atoms. The new anion is structurally characterized by single-crystal X-ray diffraction in the compound $(K[222\text{-}crypt])_4[Sn_{14}Ni(CO)]\cdot DMF$. Its presence in solution is corroborated by electrospray mass spectrometry.*

Face-fused deltahedral clusters are very rare in molecular compounds, although the phenomenon is fairly common in solids with extended structures, such as the polymorphs of elemental boron, metal borides, polar intermetallics with anionic frameworks of Ga, In, or Tl.[1,2] In the molecular world, there are two examples of face-fused deltahedral boranes, namely $[B_{21}H_{18}]^-$ and $B_{20}H_{16}(CH_3CN)_2\cdot(CH_3CN)$ in which the $[B_{21}H_{18}]^-$ is made of two fused $B_{12}$ icosahedra (coined as "twinned icosahedra") while $B_{20}H_{16}(CH_3CN)_2\cdot(CH_3CN)$ is composed of a $B_{12}$ icosahedron and a *nido*-$B_{11}$ fragment.[3,4] In addition, there are another ten or so examples of face-fused heteroboranes, such as, carboranes, metalloboranes, and that is all.[5] Despite this scarcity, however, fused clusters, especially boranes, have been of much theoretical interest in order to develop rules for rationalizing their structures, bonding, and electron counts.[6–8] In the subworld of molecular deltahedral Zintl ions, that is, main-group based anionic deltahedral clusters, face-fusion has not been observed before, although specimens of linked and vertex-fused clusters are known, for example, $[Ge_9\text{-}Ge_9]^{6-}$, $[Ge_9{=}Ge_9{=}Ge_9]^{6-}$, $[Ni_2Sn_{17}]^{4-}$, $[Ni_3@Ge_{18}]^{4-}$, $\{[Ni@Sn_8(\mu\text{-}Ge)_{1/2}]_2\}^{4-}$, $[Au_3Ge_{45}]^{9-}$, $\{Ge_{18}[Si(Si(SiMe_3))]_6\}$.[9–15] Herein we present the first example of face-fused deltahedra that is realized in the anion $[Sn_{14}Ni(CO)]^{4-}$ (**1**). It is made of two nine-atom *nido*-clusters $[Sn_8Ni(CO)]^{6-}$ that share a triangular face containing two tin and one nickel atoms (Figure 1). These conceptually novel species add to the already existing fairly large variety of tin-based clusters.[16,17]

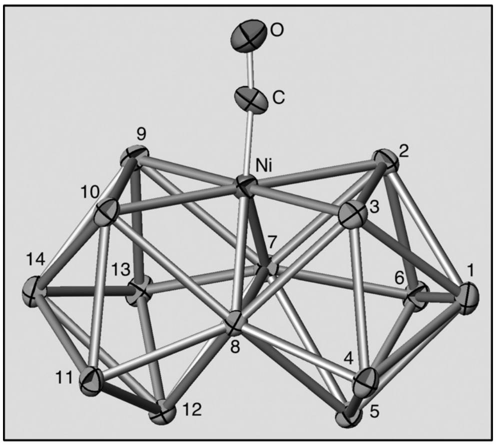

***Figure 1.*** The structure of the title anion $[Sn_{14}Ni(CO)]^{4-}$ made by face-fusion of two nine-atom deltahedra (tin atoms numbered).

The new species were discovered in the course of our studies on aggregation of known clusters by their thermal deligation and oxidation.[18] Typically, the starting clusters are heteroatomic species made of naked main-group and ligated transition-metal vertices. For example, we have already shown that such deligation by heating of small heteroatomic bismuth/nickel-carbonyl clusters leads to their aggregation to form the larger $[Bi_{12}Ni_7(CO)_4]^{4-}$ species.[19] In the present case, the substrate was the known Ni-centered Ni(CO)-capped nine-atom tin cluster $[Ni@Sn_9Ni(CO)]^{3-}$.[20] This cluster was synthesized in ethylenediamine following the previously reported procedure.[20] After removal of the solvent, the residue was redissolved in DMF and heated at 60 °C for 30 min. The presence of the new cluster anion **1** in solution was corroborated by electrospray mass spectrometry in negative-ion mode. It was observed ion-paired with $K[222\text{-}crypt]^+$ in $(K[222\text{-}crypt])Sn_{14}Ni(CO)^-$ and as the CO-free fragment $Sn_{14}Ni^-$ in addition to the parent ion observed as $(K[222\text{-}crypt])Sn_9Ni_2(CO)^-$ (Figure S1 in the Supporting Information).[21] Additional characterization was attempted by $^{119}$Sn NMR spectroscopy, but the results were inconclusive, mainly because of very fast decomposition during the experiments. Crystals with the new anion were structurally characterized by single-crystal X-ray diffraction in $(K[222\text{-}crypt])_4\mathbf{1}\cdot DMF$.

The anion is composed of two nine-atom *nido*-deltahedra $[Sn_8Ni(CO)]^{6-}$ that share a triangular face (Figure 1). Each of the nine-atom clusters is an elongated tricapped trigonal prism where one of the capping atoms is the nickel atom. The shared face involves that nickel atom and two tin atoms from a trigonal prismatic base in each of the fused clusters (atoms 7

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Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201602837.

and 8 in Figure 1). Thus, the shared face is adjacent to a trigonal-prismatic base in each of the two clusters, namely the bases made of atoms 5-7-8 in the right-hand prism and 7-8-12 in the left-hand prism. The second bases in the two prisms are made of atoms 1-2-3 and 9-10-14, respectively. Capping are atoms 4, 6, and Ni on the right, and 11, 13, and Ni on the left. The Ni-atom is coordinated by six tin atoms (2, 3, 7, 8, 9, 10) and the carbonyl group. Overall, the anion is very close to $C_{2v}$ symmetry with the two-fold axis along the Ni−CO bond. The distances related by the pseudo-symmetry differ by no more than 0.02 Å, and therefore we provide the metrics of only a half of one of the fused clusters as it is enough to describe the whole species.

First, we notice that the prismatic edges 1-5 and 2-7 are fairly long, 3.2628(10) and 3.1500(10) Å, respectively, as should be expected for a *nido*-cluster.[22] The distances at the tin-atoms 6 and 4 that cap the prism are quite normal in the range 2.8475(8)–3.0839(10) Å with the shortest distance being to the shared tin atoms 7 and 8. The trigonal prismatic base 1-2-3 that is away from the fused part is also quite typical with distances within 2.9432(10)–3.0967(9) Å, the shortest being between atoms 2 and 3 that interact with the nickel. The second triangular base, 5-7-8, on the other hand, is significantly distorted with two very long distances for 5-7 and 5-8, 3.2406(10) and 3.2174(9) Å, respectively, and a shorter one of 3.0250(9) Å for the fused 7-8 edge. Notice that 7-8 is longer than the corresponding non-shared 2-3. The elongation of 5-7 and 5-8 is most likely due to the extremely high coordination of the shared atoms 7 and 8. Lastly, the two Ni–Sn distances within the shared face, 2.5990(12) and 2.5995(12) Å for Ni–7 and Ni–8, respectively, are somewhat shorter than the distances to the trigonal prismatic bases, 2.7529(12) and 2.7319(12) Å for Ni–2 and Ni–3, respectively, but are all fairly normal compared, for example, to the average of 2.718 Å in the Ni-centered and Ni(CO) capped $[\mathrm{Ni@Sn_9Ni(CO)}]^{3-}$.[20]

The electron count of **1** is quite interesting and also educational. Often, the bonding and electron counts of naked deltahedral clusters are considered exactly equivalent with the corresponding borane deltahedra $\mathrm{B}_n\mathrm{H}_n^{m-}$, forgetting one "small" detail. This detail is that while in boranes the B−H bonding molecular orbitals (MOs) are well separated from and below the B–B cluster-bonding MOs, this is not the case for naked clusters. The corresponding lone pairs in naked clusters are well intermixed with the cluster bonding orbitals, in some cases even participating in the cluster bonding itself.[8,23,24] Thus, separating the electrons in cluster-bonding and lone-pairs is not warranted in naked clusters but is nonetheless done very often by many, including the present authors as well. Instead, the only correct electron count for such clusters should be that of the total valence electrons. The new fused cluster $[\mathrm{Sn_{14}Ni(CO)}]^{4-}$ is a very good example for this phenomenon. The available valence electrons, 14 × 4 (from Sn) + 2 (from CO) + 4 (from charge) = 62, match exactly the required number of electrons for face-fused clusters (Ni is treated as a main-group element with 0 valence electrons). The number of electrons for face-fused clusters is calculated by adding the valence electrons of each individual cluster and subtracting the number required for bonding within the common part, a triangular face in this case. Each cluster is a *nido*-species and according to Wade's rules requires $4n + 4 = 4\times 9 + 4 = 40$ valence electrons ($n$ is the number of cluster vertices). The common part, a triangle of main-group atoms that satisfy the octet rule, requires $3\times 6 = 18$ valence electrons. Thus, the fused species requires $2\times 40 - 18 = 62$ valence electrons, which is exactly the number of available electrons.

Apportioning the 62 valence electrons to cluster-bonding electrons and lone-pair electrons, however, fails. Thus, the commonly accepted approach introduced by Jemmis et al. prescribes $2(m+n+p)$ required bonding electrons where $m$ is the number of fused clusters, $n$ is the number of vertices in the resulting species, and $p$ is the number of missing vertices in each of the fused clusters.[6] In our case these numbers are 2, 15, and 2, respectively, for $m$, $n$, and $p$, and thus $2(2 + 15 + 2) = 38$ cluster bonding electrons. Assuming that all but the two shared tin atoms have electron lone-pairs and accounting for the 2 electrons for the Ni-CO *exo*-bond, we get additional $12\times 2 + 2 = 26$ required electrons. This totals 64, which means that two more electrons are required than those available. Where is the problem in this electron counting? Clearly, it is in the assumption that all non-shared tin atoms have lone pairs of electrons that do not participate in the cluster bonding.

A closer look at the metrics of $[\mathrm{Sn_{14}Ni(CO)}]^{4-}$ reveals that the two constituting clusters have one unreasonably short *inter*-cluster distance, that between tin atoms 5 and 12 at 3.4878(11) Å (Figure 1). This distance is not much longer than some of the *intra*-cluster distances, for example, 3.2628(10) for 1–5. Burdett and Canadell have already demonstrated that lone-pair orbitals in such close-proximity atoms from fused clusters or on sufficiently flat surfaces of large clusters can interact strongly enough to push the antibonding combination high in energy above the HOMO–LUMO gap.[25] In other words, one of the two lone-pairs formally becomes empty, and its electrons are used for cluster bonding instead. A previously reported example of the phenomenon is the 18-atom deltahedron found in the intermetallic $\mathrm{Na_{49}Cd_{58.5}Sn_{37.5}}$ where pairs of atoms are on fairly flat surface and their lone pairs interact strong enough to leave some of them empty.[26] The DFT calculations on $[\mathrm{Sn_{14}Ni(CO)}]^{4-}$ with optimized geometry confirmed the observed charge by showing a fairly large HOMO–LUMO gap of 1.87 eV. The analysis of the molecular orbitals, focusing specifically on atoms 5 and 12, did not lead to clear choice of bonding and antibonding combination of the radial orbitals at these atoms since, as discussed above, they are all intermixed playing both bonding and lone-pair functions. However, there is a possible pair of such orbitals where the antibonding combination is empty while the bonding is filled (Figure S2). Of course, the cluster's symmetry guarantees considerable mixing of these orbitals with a number of other atoms in the cluster.

Of interest is also the nature of the nickel-cluster interactions viewing the cluster as a ligand to the organometallic Ni(CO) moiety. Analysis of the DFT results clearly identified three filled orbitals where the Ni(CO) fragment interacts with the cluster in one σ and two π interactions (Figure 2). Thus, as seen in many other cases, the cluster acts as a six-electron ligand and completes the 18-electron

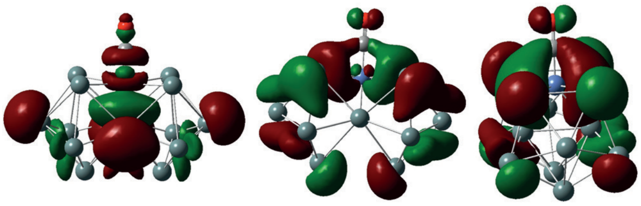

**Figure 2.** Ni-(CO) fragment interactions with $Sn_{14}^{4-}$ cluster, consisting of one σ (left) and two π combinations (middle and right). Sn gray spheres, Ni pale blue, O red, C small gray sphere.

environment around the nickel atom.[27] Other examples are $E_9[ZnPh]^{3-}$ (E = Si, Ge, Sn, Pb) and $E_9[M(CO)_3]^{4-}$ (E = Sn, Pb; M = Cr, Mo, W) with the transition-metal coordinated to the square face of the $E_9$ cluster.[27]

The new fused species $[Sn_{14}Ni(CO)]^{4-}$ is a unique member in the list of heteroatomic group-14/transition-metal large clusters such as the elegant cages of $[M@Ge_{10}]^{3-}$ (M = Fe, Co), $M@Pb_{12}^{2-}$ (M = Ni, Pd, Pt), $Mn@Pb_{12}^{3-}$, $Pd_2@Sn_{18}^{4-}$, $Pt_2Sn_{17}^{4-}$, $Ni_2Sn_{17}^{4-}$, $Ir@Sn_{12}^{3-}$, and $Ni@Sn_{12}^{2-}$.[16] The mechanism of how these species form is not well understood at this stage. Nonetheless, the recent isolation of $TiCp(Sn_8)^{3-}$ alongside $Cp_5Ti_4Sn_{15}^{n-}$ ($n = 4, 5$) gives a glimpse of how a $Sn_8$ fragment could be the possible intermediate in the formation of the larger species.[28] In our case, it seems that $[Sn_{14}Ni(CO)]^{4-}$ is assembled of fragments generated by the heat-driven fragmentation and eventual oxidation of the parent cluster $[Ni@Sn_9Ni(CO)]^{3-}$. The new fused cluster can be viewed as an intermediate between the parent cluster and the final elemental tin, which is the only product after longer heating. Very likely, there are other intermediates that could be eventually isolated by other techniques. What is clear, however, is that transition metals seem to "stabilize" unusual fragments and/or larger main-group clusters, for example $Ge_8[Mo(CO)_3]_2^{4-}$, $Pb_5[(Mo(CO)_3)_2]^{5-}$, $Sn_6[Nb(Tol)]_2^{2-}$.[16,29]

## Experimental Section

*Materials* All reactions and materials were handled under inert atmosphere or vacuum using standard Schlenk-line or glove box techniques. Ethylenediamine (*en*) was distilled over sodium metal and stored in a gastight ampoule under nitrogen. 2.2.2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo [8.8.8]hexacosane, Sigma Aldrich, 98 %), *N,N*-Dimethylformamide (*DMF)* (Anhydrous, EMD Millipore 99.8 %) and bis(triphenylphosphine)nickeldicarbonyl (Strem, 98 %) were used as received. Toluene (Alfa-Aesar, 99.8+ %) was dried by passing over a copper based catalyst and 4 Å molecular sieves and then stored in gastight ampoule under nitrogen. $K_4Sn_9$ was synthesized from the elements (K cubes: Sigma Aldrich 99.5 %, surfaces shaved before use, Sn Shot: Strem, 99.8 %) at 950 °C for 2 days in sealed niobium tubes then evacuated within a fused silica jacket.

*Synthesis of (K[crypt])$_4$Sn$_{14}$(Ni-CO)·DMF (**1**)*: $K_4Sn_9$ (63 mg, 0.051 mmol) and crypt (89 mg, 0.236 mmol) were weighed out into a test tube and dissolved using 2 mL *en*. After a few minutes $Ni(PPh_3)_2(CO)_2$ (77 mg, 0.120 mmol) were added directly to the solution. This solution was then stirred for 3 h before removal of *en* under vacuum. The resulting residue is then washed with toluene (ca. 10 mL) followed by dissolution in 2 mL DMF. The brown-red solution is then heated at 60 °C for 30 min in a silicon oil bath. The reaction mixture is then allowed to cool to room temperature for another 30 min. The reaction mixture is centrifuged, filtered, and the filtrate layered with toluene. After a few days brown-red blocks of (**1**) formed (5 % c.a. by crystals) alongside a gray precipitate, a brown precipitate, and a metallic mirror.

*Structure determination.* Single crystal X-ray diffraction data were obtained on a Bruker APEX-II diffractometer equipped with a curved graphite monochromator and a CCD area detector using MoKα radiation at 120 K. The crystal was mounted on a Mitegen micromount loop after selection from Paratone-N oil and positioned under a nitrogen cold stream. The structure was solved using SHELXT and refined on $F^2$ against all reflections using SHELXL2014.[30] Crystal data: monoclinic $P\bar{1}$ $a = 15.146(3)$, $b = 16.270(3)$, $c = 25.233(5)$ Å, $\alpha = 88.683(3)$, $\beta = 89.837(3)$, $\gamma = 71.404(3)°$, $V = 5892(2)$ Å$^3$, $Z = 2$, $R1/wR2 = 0.0535/0.1520$ for the observed data and $R1/wR2 = 0.0798/0.1636$ for all data. CCDC 1469503 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

*Mass Spectrometry.* ES-MS spectra were collected on a Micromass Quattro-LC triple-quadrupole mass spectrometer (125 °C source temperature, 150 °C desolvation temperature, 2.5 kV capillary voltage and 30 V cone voltage.) **1** was dissolved in DMF and introduced using a Harvard syringe pump at 10 μL min$^{-1}$ via direct infusion.

*Electronic Structure Calculations.* DFT calculations were conducted on **1** in order to rationalize its stability. Single point energy calculations were carried out using Becke three-parameter density functional with the Lee–Yang–Parr correlation (B3LYP) with the LanL2DZ basis set.[31] The calculations were performed using the Gaussian 09 package.

## Acknowledgements

We thank the financial donation by Dr. Joseph Y. Chang for partial support of this research.

**Keywords:** cluster compounds · nickel · tin · Zintl anions

**How to cite:** *Angew. Chem. Int. Ed.* **2016**, *55*, 6721–6724
*Angew. Chem.* **2016**, *128*, 6833–6836

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Received: March 21, 2016