The Elusive \( \text{closo-Ge}_{10}^{2-} \) Zintl Ion: Finally “Captured” as a Ligand in the Complex \([\text{Ge}_{10}\text{Mn(CO)}_{4}]^{3-}\)

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Although often seen in mass spectra, the otherwise elusive closo-\( \text{Ge}_{10}^{2-} \) Zintl ion has been finally structurally characterized as coordinated to manganese in \([\text{Ge}_{10}\text{Mn(CO)}_{4}]^{3-}\) made by the reaction of \( \text{nido-Ge}_{9}^{4-} \) with \([\text{Mn(CO)}_{10}]\) in ethylenediamine. The new cluster is a bicapped square antiprism, as expected for a closo-deltahedron of 10 atoms.

Fragmentation of the well-known nine-atom \( \text{nido} \)-deltahedral Zintl ions of group 14, \( \text{Ge}_{9}^{4-}, \text{Sn}_{9}^{4-} \), and \( \text{Pb}_{9}^{4-} \), is not an uncommon phenomenon, especially for the heavier congeners, and is manifested by the observed reassembly of the fragments into larger clusters. Thus, the reactions of \( \text{Pb}_{9}^{4-} \) clusters with \([\text{Pt(PPh}_{3})_{4}]^{2-}\) and \([\text{Ni}(@\text{Pb}_{10}]^{2-}\), and 10-atom bicapped prisms, \([\text{Ni}(@\text{Pb}_{10}]^{2-}\), respectively.1,2 Similarly, the reactions of nine-atom \( \text{Sn}_{9}^{4-} \) clusters with \([\text{Ni}(@\text{COD}]^{2-}\) and \([\text{COD}][\text{IrCl}]_{2}\) lead to the 17-atom species \([\text{Ni}_{2}\text{Sn}_{17}]^{4-}\) with a complex structure and the icosahedral \([\text{Ir}(@\text{Sn}_{12}]^{3-}\) (after oxidation of the initially formed and structurally characterized \([\text{Sn}_{9}\text{Ir(COD)}]^{3-}\)), respectively.3–5 The recent synthesis of ferrocene-like \([\text{Fe}(@\text{Ge}_{10}]^{3-}\) and \([\text{Co}(@\text{Ge}_{10}]^{3-}\) from \( \text{Ge}_{9}^{4-} \) ions showed that germanium is not immune to such fragmentations either.6,7 What is common in all these reactions is that they all contain a central transition metal, and the product is not a nine-atom cluster or a multiple of it as in, for example, \([\text{Ni}_{3}\text{Ge}_{18}]^{4-}\) and \([\text{Pd}_{3}\text{Ge}_{18}]^{4-}\).8,9 The mechanisms for the formation of these species must involve some fragmentation of the nine-atom clusters, perhaps driven by nucleation of the larger clusters around the central transition metals.10 However, the successful synthesis and characterization of \( \text{closo-Pb}_{10}^{2-} \) by soft oxidation of \( \text{Pb}_{9}^{4-} \) with \( \text{Au(I)} \) salt indicates that such a central atom is not always necessary.11 This is further supported by the observed formation of heteroatomic nine-atom clusters \( \text{Ge}_{9-x}\text{Sn}_{x}^{4-} \) (\( x = 0–9 \)) from the corresponding homoatomic \( \text{Ge}_{9}^{4-} \) and \( \text{Sn}_{9}^{4-} \), which presumably involves fragmentation and reassembly as well.12

The same mechanism is most likely responsible for the formation of the 10-atom germanium species often observed in our electrospray mass spectra. Thus, the reactions of \( \text{Ge}_{9}^{4-} \) clusters (derived from the intermetallic precursor \( \text{K}_{4}\text{Ge}_{9} \)) with aldehydes and ketones in dimethylformamide (DMF) exhibit almost exclusively a peak at \( m/z = 727 \) which corresponds to \( \text{Ge}_{10}^{4-} \).13 Clearly, some oxidation and fragmentation of \( \text{Ge}_{9}^{4-} \) must take place in such reactions. However, our numerous attempts to crystallize and structurally characterize this elusive 10-atom cluster by employing different solvents and cation sequestering agents had been unsuccessful until now. Here, we report the isolation and structure of the deltahedral \( \text{closo-Ge}_{10}^{2-} \) Zintl ion as a ligand in the manganese tetracarbonyl complex \([\text{Ge}_{9}\text{Mn(CO)}_{4}]^{3-}\) (Figure 1).

The new compound, \([\text{K}(2,2,2\text{-crypt})][\text{Ge}_{10}\text{Mn(CO)}_{4}]\)·tol, was crystallized as dark purple blocks from the soft oxidation of \( \text{Ge}_{9}^{4-} \) in an ethylenediamine solution of \( \text{K}_{4}\text{Ge}_{9} \) with \( \text{Mn}_{2}^{4-} \) in the presence of \( 2,2,2\)-crypt. Some of the purple crystals were dissolved in DMF, and the resulting light purple solution was used for carrying out electrospray mass spectrometry in the negative-ion mode. The spectra (in the Supporting Information) showed not only the \([\text{Ge}_{10}\text{Mn(CO)}_{4}]^{3-}\) anion at \( m/z = 894 \) but also its derivatives after the loss of one or more carbon monoxide ligands in the process of solvent removal, i.e., \([\text{Ge}_{10}\text{Mn(CO)}_{5}]^{3-}\), \([\text{Ge}_{10}\text{Mn(CO)}_{6}]^{3-}\), \([\text{Ge}_{10}\text{Mn(CO)}_{7}]^{3-}\), and \([\text{Ge}_{10}\text{Mn}]^{3-}\) at \( m/z = 866, 838, 810, \) and 782, respectively.

(13) Schneeberger, P. M. In Functionalization and Reactivity of Germanium Clusters, M.S. Thesis, University of Notre Dame, Notre Dame, IN, 2009.
Although a much earlier report claims the synthesis of Ge$_{10}^{2–}$, the structure reported there is so greatly disordered that even the identity of the cluster is uncertain, and the cluster has been widely viewed to be the nine-atom closo-Ge$_9^{2–}$, which prescribes 4$n$ + 2 electrons for closo-deltahedra with $n$ vertices. Its geometry, as expected for a 10-atom closo-deltahedron, is that of a bicapped square antiprism with pseudo-D$_{4d}$ symmetry. The distances with the cluster are very similar to other analogous species with 10 vertices and the same electron count, e.g., [Ge$_9$Zn-Ph]$^{3–}$ with the same geometry (Zn is one of the capping atoms) and 42 cluster electrons (9 × 4 from Ge + 2 from Zn + 1 from Ph + 3 from charge). The three types of distances can be defined depending on the types of atoms they connect, and their averages in Ge$_{10}^{2–}$ are as follows: 2.575 Å at the capping atoms, 2.547 Å between the staggered squares, and 2.812 Å within the squares.

In [Ge$_{10}$Mn(CO)$_4$]$^{3–}$, the closo-Ge$_{10}^{2–}$ cluster coordinates to the Mn center via the lone pair of one of the capping atoms of the bicapped square antiprism and thus acts as a normal two-electron ligand. From an organometallic point of view, the Mn center itself achieves an 18-electron configuration by combining the electrons from five ligands (four CO and one cluster), the metal center with seven electrons, and one negative charge, i.e., [{Ge$_{10}$}Mn(CO)$_4$]$^{3–}$ (HOMOs are $d_{x^2}$ and $d_{x^2–y^2}$ on Mn, nearly degenerate). Thus, the −3 charge of the complex can be viewed as distributed between the cluster and the Mn center. The Mn–Ge distance of 2.3347(8) Å cannot be compared with that in a similar anionic complex because there are none available. The only available related compound is the 19-electron complex (CF$_3$)$_2$GeMn(CO)$_5$, and its Ge–Mn distance of 2.4132(9) Å is understandably quite longer.

The infrared spectrum of the new compound (crystals in Nujol) showed the C–O stretching modes at very low frequencies of 1892, 1789, and 1775 cm$^{-1}$. As expected, they are lower than those in neutral species such as HMn(CO)$_5$ (2094, 2001, and 1970 cm$^{-1}$) and Mn$_2$(CO)$_{10}$ (2044, 2013, and 1983 cm$^{-1}$), but they are also lower than the frequencies of even the anionic [Mn(CO)$_5$]$^{2–}$ (1893 and 1860 cm$^{-1}$) and [Ph$_3$P]Mn(CO)$_4$] (1940, 1846, and 1815 cm$^{-1}$). This suggests very strong electron donation from the negatively charged cluster to the Mn center and subsequently to the carbonyls’ π* orbitals. This is supported further by the much shorter Mn–C and much longer C–O distances in [Ge$_9$–Mn(CO)$_4$]$^{3–}$, 1.784 and 1.161 Å (averaged), respectively, when compared with both the neutral and the anionic species: $d_{Mn–C}$/d$_{C–O}$(av.) = 1.847/1.123, 1.846/1.130, 1.798/1.156, and 1.796/1.159 Å in HMn(CO)$_5$, Mn$_2$(CO)$_{10}$, [Mn$_2$(CO)$_{10}$] (Aldrich, 99%) were used as received after carefully heating a stoichiometric mixture of the elements (K: 99% for an additional 3 h. The resulting dark purple solution was filtered from the substantial amount of precipitate (most likely clusters oxidized to neutral Ge) and layered with toluene.

All operations were carried out under an inert atmosphere or vacuum using standard Schlenk-line or glovebox techniques. Ethylenediamine (Alfa-Aesar, 99%) was distilled over sodium metal and stored in a gastight ampule under nitrogen in the glovebox. Dried toluene was stored over molecular sieves in the glovebox. 2,2-Crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, Acros, 98%) and Mn$_2$(CO)$_{10}$ (Aldrich, 99%) were used as received after carefully drying them under a vacuum. K$_4$Ge$_9$ was synthesized by heating a stoichiometric mixture of the elements (K: 99%+, Strem; Ge: 99.999%, Alfa Aesar) at 900 °C for 2 days in sealed niobium containers jacketed in evacuated fused silica ampules. K$_4$Ge$_9$ (70 mg, 0.086 mmol) and 2,2-crypt (129 mg, 0.344 mmol) were dissolved in 2 mL of ethylenediamine (red solution) in a test tube inside a glovebox. Mn$_2$(CO)$_{10}$ (130 mg, 0.112 mmol) was added, and the reaction mixture was stirred for an additional 3 h. The resulting dark purple solution was filtered from the substantial amount of precipitate (most likely clusters oxidized to neutral Ge) and layered with toluene. It yielded nicely shaped black-purple block crystals of [K(2,2,2-crypt)]$_2$[Ge$_{10}$Mn(CO)$_{12}$]·tol after 2 weeks (ca. 46% crystalline yield).

Single-crystal X-ray diffraction data of [K(2,2,2-crypt)]$_2$[Ge$_{10}$Mn(CO)$_{12}$]·tol were collected on a Bruker APEX diffractometer with a CCD area detector and Mo Kα radiation at 100 K. The structure was solved by direct methods and was refined on $F^2$ using the SHELXTL V5.1 package. Crystal data: monoclinic, $P2_1/n$, $a = 15.3123(6)$, $b = 20.9401(8)$, $c = 9.5557(4)$ Å, $\beta = 112.001(2)$°, $V = 2768.5(3)$ Å$^3$, $Z = 4$, $D_x = 1.874$ g/cm$^3$. The crystal structure analysis showed that the Ge$_{10}$Mn(CO)$_{12}$ ion is a deltahedron with 42 electrons (two each of K, Mn, and CO). The Ge$_{10}$Mn(CO)$_{12}$ ion is a deltahedron with 42 electrons (two each of K, Mn, and CO). The Ge$_{10}$Mn(CO)$_{12}$ ion is a deltahedron with 42 electrons (two each of K, Mn, and CO). The Ge$_{10}$Mn(CO)$_{12}$ ion is a deltahedron with 42 electrons (two each of K, Mn, and CO).
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c = 28.0514(11) Å, β = 92.818(2)°, V = 8983.6(6) Å³, Z = 4, 
R1/wR2 = 4.12/9.51% for the observed data (I > 2σ(I)), R1/ 
wR2 = 6.56/10.53% for all data.

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Supporting Information Available: X-ray crystallographic file in CIF format and electrospray mass spectrum in negative ion mode of [K(2,2,2-crypt)][Ge10Mn(CO)4]·tol are available free of charge via the Internet at http://pubs.acs.org.