6396 *Inorg. Chem.* **2010**, *49*, 6396–6398
DOI: 10.1021/ic100877u

Inorganic Chemistry
Communication

The Elusive *closo*-Ge_{10}^{2-} Zintl Ion: Finally "Captured" as a Ligand in the Complex $[Ge_{10}Mn(CO)_4]^{3-}$

Daniel Rios and Slavi C. Sevov*

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556

Received May 4, 2010

Although often seen in mass spectra, the otherwise elusive *closo*-Ge_{10}^{2-} Zintl ion has been finally structurally characterized as coordinated to manganese in $[Ge_{10}Mn(CO)_4]^{3-}$ made by the reaction of *nido*-Ge_9^{4-} with $Mn_2(CO)_{10}$ 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 *nido*-deltahedral Zintl ions of group 14, Ge_9^{4-}, Sn_9^{4-}, and 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 Pb_9^{4-} clusters with $[Pt(PPh_3)_4]$ and $Ni(COD)_2$ result in 12-atom icosahedra, $[Pt@Pb_{12}]^{2-}$, and 10-atom bicapped prisms, $[Ni@Pb_{10}]^{2-}$, respectively.[1,2] Similarly, the reactions of nine-atom Sn_9^{4-} clusters with $Ni(COD)_2$ and $[(COD)IrCl]_2$ lead to the 17-atom species $[Ni_2Sn_{17}]^{4-}$ with a complex structure and the icosahedral $[Ir@Sn_{12}]^{3-}$ (after oxidation of the initially formed and structurally characterized $[Sn_9Ir(COD)]^{3-}$), respectively.[3-5] The recent synthesis of ferrocene-like $[Fe@Ge_{10}]^{3-}$ and $[Co@Ge_{10}]^{3-}$ from 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, $[Ni_3Ge_{18}]^{4-}$ and $[Pd_2Ge_{18}]^{4-}$.[8,9] The mechanisms for the formation of these species most likely 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 *closo*-Pb_{10}^{2-} by soft oxidation of Pb_9^{4-} with 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 $Ge_{9-x}Sn_x^{4-}$ ($x = 0-9$) from the corresponding homoatomic Ge_9^{4-} and 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 Ge_9^{4-} clusters (derived from the intermetallic precursor K_4Ge_9) with aldehydes and ketones in dimethylformamide (DMF) exhibit almost exclusively a peak at $m/z = 727$ which corresponds to Ge_{10}^{-}.[13] Clearly, some oxidation and fragmentation of 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 *closo*-Ge_{10}^{2-} Zintl ion as a ligand in the manganese tetracarbonyl complex $[Ge_{10}Mn(CO)_4]^{3-}$ (Figure 1).

The new compound, $[K(2,2,2\text{-crypt})]_3[Ge_{10}Mn(CO)_4]\cdot$tol, was crystallized as dark purple blocks from the soft oxidation of Ge_9^{4-} in an ethylenediamine solution of K_4Ge_9 with $Mn_2(CO)_{10}$ 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 $[Ge_{10}Mn(CO)_4]$ 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., $[Ge_{10}Mn(CO)_3]$, $[Ge_{10}Mn(CO)_2]$, $[Ge_{10}Mn(CO)]$, and $[Ge_{10}Mn]$ at $m/z = 866$, 838, 810, and 782, respectively.

---

*To whom correspondence should be addressed. E-mail: ssevov@nd.edu.

[1] Esenturk, N. E.; Fettinger, J.; Lam, Y.; Eichhorn, B. *Angew. Chem., Int. Ed.* **2004**, *43*, 2132.

[2] Esenturk, N. E.; Fettinger, J.; Eichhorn, B. *Chem. Commun.* **2005**, 247.

[3] Esenturk, N. E.; Fettinger, J.; Eichhorn, B. *J. Am. Chem. Soc.* **2006**, *128*, 12.

[4] Downing, D. O.; Zavalij, P.; Eichhorn, B. W. *Eur. J. Inorg. Chem.* **2010**, 890.

[5] Wang, J. Q.; Stegmaier, S.; Wahl, B.; Fässler, T. F. *Chem.—Eur. J.* **2010**, *16*, 1793.

[6] Zhou, B.; Denning, S. M.; Kays, L. D.; Giocoechea, J. M. *J. Am. Chem. Soc.* **2009**, *131*, 2802.

[7] Wang, J. Q.; Stegmaier, S. D.; Fässler, T. F. *Angew. Chem., Int. Ed.* **2009**, *121*, 2032.

[8] Goicoechea, J. M.; Sevov, S. C. *Angew. Chem., Int. Ed.* **2005**, *44*, 4026.

[9] Goicoechea, J. M.; Sevov, S. C. *J. Am. Chem. Soc.* **2005**, *127*, 7676.

[10] Fässler, T. F.; Hoffmann, S. D. *Angew. Chem., Int. Ed.* **2004**, *43*, 6242.

[11] Spiekermann, A.; Hoffmann, S. D.; Fässler, T. F. *Angew. Chem., Int. Ed.* **2006**, *45*, 3459.

[12] Gillett-Kunnath, M. M.; Petrov, I.; Sevov, S. C. *Inorg. Chem.* **2010**, *49*, 721.

[13] Schneeberger, P. M. In *Functionalization and Reactivity of Germanium Clusters*, M.S. Thesis, University of Notre Dame, Notre Dame, IN, 2009.

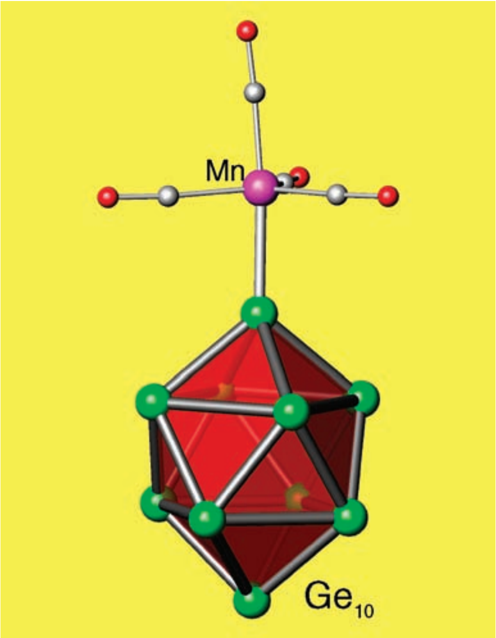

Figure 1. The complex anion $[Ge_{10}Mn(CO)_4]^{3-}$ is composed of a deltahedral *closo*-Ge_{10}^{2-} Zintl ion coordinated as a ligand to a $Mn(CO)_4^-$ fragment to form an 18-electron Mn complex (d_{Ge-Mn} = 2.335 Å). The Ge_{10}^{2-} ion is a bicapped square antiprism with average Ge−Ge distances (Å) of 2.575 at the capping atoms, 2.547 between the staggered squares, and 2.812 within the squares.

Although a much earlier report claims the synthesis of Ge_{10}^{2-},[14] the structure reported there is so greatly disordered that even the nuclearity of the cluster is uncertain, and the cluster has been widely viewed to be the nine-atom *closo*-Ge_9^{2-}.[15]

Ge_{10}^{2-} is a 10-atom deltahedron with 42 electrons (four from each germanium and two from the charge), and as such it satisfies Wade-Mingos' rule for a *closo*-deltahedron, which prescribes $4n + 2$ 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., $[Ge_9Zn\text{-}Ph]^{3-}$ 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).[16] 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. For comparison, the corresponding distances in $[Ge_9Zn\text{-}Ph]^{3-}$ are 2.564 (at the only one Ge capping atom), 2.551, and 2.804 Å.

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., $[(Ge_{10}^{2-})Mn(CO)_4]^-$ (HOMOs are d_{xy} 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 $(CF_3)_3GeMn(CO)_5$, and its Ge−Mn distance of 2.4132(9) Å is understandably quite longer.[17]

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}),[18,19] but they are also lower than the frequencies of even the anionic $[Mn(CO)_5]^-$ (1893 and 1860 cm^{-1}) and $[(Ph_3P)Mn(CO)_4]^-$ (1940, 1846, and 1815 cm^{-1}).[20] 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 $[Ge_9\text{−}Mn(CO)_4]^{3-}$, 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 1.796/159 Å in $HMn(CO)_5$,[21] $Mn_2(CO)_{10}$,[22] $[Mn(CO)_5]^-$,[23] and $[(Ph_3P)Mn(CO)_4]^-$,[24] respectively.

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. 2,2,2-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_4Ge_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_4Ge_9 (70 mg, 0.086 mmol) and 2,2,2-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 $[K(2,2,2\text{-crypt})]_3[Ge_{10}Mn(CO)_4]\cdot$tol after 2 weeks (ca. 46% crystalline yield).

Single-crystal X-ray diffraction data of $[K(2,2,2\text{-crypt})]_3[Ge_{10}Mn(CO)_4]\cdot$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), and

---

[14] Belin, C.; Mercier, H.; Angilella, V. *New J. Chem.* **1991**, *15*, 931.

[15] Fässler, T. F.; Hunzkiker, M.; Spahr, M.; Lueken, H. *Z. Anorg. Allg. Chem.* **2000**, *626*, 692.

[16] Goicoechea, J. M.; Sevov, S. C. *Organometallics* **2006**, *25*, 4530.

[17] Brauer, J. D.; Eujen, R. *Organometallics* **1983**, *2*, 263.

[18] Rest, A. J.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1969**, 375.

[19] Flitcroft, N.; Huggins, D. K.; Kaesz, H. D. *Inorg. Chem.* **1964**, *3*, 1123.

[20] Faltynek, R. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, 2701.

[21] La Placa, S. J.; Hamilton, W. C.; Ibers, J. A.; Davison, A. *Inorg. Chem.* **1969**, *8*, 1928.

[22] Churchill, M. R.; Amoh, K. N.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1609.

[23] Corraine, M. S.; Lai, C. K.; Zhen, Y.; Churchill, M. R.; Buttrey, L. A.; Ziller, J. W.; Atwood, J. D. *Organometallics* **1992**, *11*, 35.

[24] Riley, O. E.; Davis, R. E. *Inorg. Chem.* **1980**, *19*, 159.

$c = 28.0514(11)$ Å, $\beta = 92.818(2)°$, $V = 8983.6(6)$ Å^3, $Z = 4$, R1/wR2 = 4.12/9.51% for the observed data ($I > 2\sigma(I)$), R1/wR2 = 6.56/10.53% for all data.

Acknowledgment. This material is based upon work supported by the Department of Energy, Office of Basic Energy Sciences, under Award Number DE-FG02-07ER46476. We thank M. M. Gillett-Kunnath for helping with the IR spectra.

Supporting Information Available: X-ray crystallographic file in CIF format and electrospray mass spectrum in negative ion mode of $[K(2,2,2\text{-crypt})]_3[Ge_{10}Mn(CO)_4]\cdot$tol are available free of charge via the Internet at http://pubs.acs.org.