[Ni-Ni-Ni@Ge9]4+: A Linear Triatomic Nickel Filament Enclosed in a Dimer of Nine-Atom Germanium Clusters**

Jose M. Goicoechea and Slavi C. Sevov*

The chemistry of nine-atom deltahedral Zintl anions of Group 14 has advanced greatly in recent years. Redox reactions of these clusters have led to dimers, trimers, tetraters, and infinite chains of germanium clusters such as [Ge2GeGe]4–,[1] [Ge3GeGeGe]4–,[2] [Ge5GeGeGeGe]6–,[3,4] \(-\{\text{Ge9}\}^2\)-,[5,6] and \(-\{\text{HGe9}\}^2\)-.[7] Similar redox reactions combined with nucleophilic addition of various anions have produced, for the first time, substituted clusters such as [Ge2SnPh3]4–, [PhSnGeGeGeSnPh3]2–, [Ph3SbGeGeSbPh2]2–, and [Ph3SnGeGeGeSnPh3]3–.[8–10] Also, it has been known for quite some time that ligand-exchange reactions with organo-metallic compounds can add a transition-metal vertex to the cluster and form species such as [SnM(CO)3]4– for M = Cr, Mo, W.[11–13] More recent experiments with [Pt(PPh3)4], [Ni(CO)2(PPh3)2], and [Ni(cod)] (cod = 1,5-cyclooctadiene) have shown that the nine-atom cluster can accommodate a central transition-metal atom to form \([\text{Ni@Ge9Ni-PPh3}]^2\)-.[14] \([\text{Ni@}(\text{Sn9Ni}-\text{CO})]^2\)-, and \([\text{Pt@}(\text{Sn9Pt}-\text{PPh3})]^2\)-.[15] Note that these species also contain a ligated transition-metal atom in the form of (Ni-PPh3), [Ni-CO], or [Pt-PPh3] fragments as a vertex of the cluster and are thus ten-atom clusters. Similar reactions involving Pb3 clusters resulted in cluster enlargement and formation of the first ligand-free, transition-metal centered deltahedral clusters \([\text{Ni@Ph3}]^2\)- and \([\text{Pt@Ph3}]^2\)- with the shapes of a bicapped square antiprism and an icosahedron, respectively.[16,17] Also, a reaction of the As3+ ions with [Ni(cod)]3+ leads to a large cluster of 20 arsenic atoms around an arsenic-centered [Ni3] core.[18]

Herein we report the synthesis and characterization of a ligand-free anion that contains a linear trimer of nickel enclosed inside two nine-atom germanium clusters, [Ni-Ni-Ni@Ge9]4+ (I; Figure 1). This compound is the first ligand-free deltahedral formation of Group 14 with more than one transition-metal atom inside. The anion was structurally characterized in the species \([\text{K}(2,2,2\text{-crypt})][\text{Ni@Ge9}]\)2·2tol (2,2,2-crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[9.8.8]hexacosane, tol = toluene) made in a high yield by a reaction of an ethylenediamine(ethyl) solution of K4Ge9 with a threefold excess of [Ni(cod)]3+.

The two end atoms of the nickel trimer center the two nine-atom germanium clusters while the central nickel atom is positioned at an inversion center and plays the role of a tenth (shared) vertex for each cluster. A closer look at the nine-atom germanium clusters reveals that, similar to many empty clusters, they can be described as distorted tricapped trigonal prisms (Figure 1). Typically, the distortion in empty clusters is expressed in elongation of one, two, or all three of the vertical prismatic edges 1-7, 2-8, and 3-9. The nickel-centered clusters in I show the same distortion, all three edges being significantly longer, 3.061(2), 3.052(2), and 3.016(2) Å, than the remaining Ge–Ge distances, 2.604(1)–2.749(2) Å. However, the clusters in I are additionally distorted by the opening of one of the triangular bases of the prisms, the base made of atoms 7-8-9. This distortion is clearly caused by the insertion of the additional nickel atom, Ni2, as a vertex of the two nine-atom germanium clusters (Figure 1) and results in two nickel-centered ten-atom clusters made of one nickel and nine germanium atoms, [Ni@Ge9Ni]. The two clusters form a dimer by sharing the nickel vertex, and the formula of I can be

**

[*] J. M. Goicoechea, Prof. S. C. Sevov
Department of Chemistry and Biochemistry
University of Notre Dame
Notre Dame, IN 46556 (USA)
Fax: (+1) 574-631-6652
E-mail: ssevov@nd.edu

[**] This work was supported by the National Science Foundation (CHE-0446131). We thank Bill Boggess for helping with the mass spectrometry.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.
written as \([\text{Ni}(@\text{Ge}_9)\text{Ni}(@\text{Ge}_9)]^{2-}\). Interestingly, the corresponding monomer, \([\text{Ni}(@\text{Ge}_9\text{Ni-PPh}_3)]^{2-}\), also exists, as mentioned above, and has exactly the same shape (as does \([\text{Pt}@(@\text{Sn}_9\text{Pt-PPh}_3)]^{2-}\) as the \([\text{Ni}(@\text{Ge}_9\text{Ni}])\) unit of \(I\). The only difference is that the outer nickel atom in 2 is ligated (Figure 2b). The monomer, in turn, can be viewed as being made by insertion of a Ni–L fragment along the pseudo threefold axis of a hypothetical nickel-centered \([\text{Ni}(@\text{Ge}_9)]\) tricapped trigonal prism and opening of the corresponding triangular base (Figure 2). We searched for these hypothetical species by carrying out reactions of \(\text{Ge}_9\) clusters (\(\text{K}_4\text{Ge}_9\) dissolved in ethylenediamine) with smaller excesses of \([\text{Ni(cod)}]_2\). These reactions were successful in \([\text{K}(@\text{2,2,2-crypt})]_4-\) \([\text{Ni}(@\text{Ge}_9\text{Ni-PPh}_3)]^{2-}\) (2) ion can be viewed as being made from \([\text{Ni}(@\text{Ge}_9)]^{2-}\) by insertion of an Ni–L fragment and opening of one of the bases of the trigonal prism.

![Figure 2.](image)

Also very similar, 2.361 Å. The only other linear trimer of metal atoms that are part of fused clusters happens to be a ruthenium trimer in \([\text{Cp}^*\text{RuB}_4\text{H}_{10}\text{Ru(Cp}^*\text{RuB}_4\text{H}_6)]\). Each cluster in this case is a pentagonal pyramid with a \([\text{Cp}^*\text{Ru}]\) moiety at its apex and a shared ruthenium atom in the base (the clusters are shared in a transoid fashion giving linear Ru-Ru-Ru). Furthermore, as with 2, the corresponding monomeric cluster \([\text{Cp}^*\text{RuB}_4\text{H}_6\text{Ru-Cp}^*]\) is also known.

The charge of 4 of \(I\) can be understood as the sum of the charges of \([\text{Ni}(@\text{Ge}_9\text{Ni-L})]^{2-}\) and \([\text{Ni}(@\text{Ge}_9)]^{2-}\). The latter formally replaces the ligand \(L\) in the former, that is, \([\text{Ni}(@\text{Ge}_9\text{Ni-L})]^{2-} + [\text{Ni}(@\text{Ge}_9)]^{2-} \rightarrow [\text{Ni}(@\text{Ge}_9\text{NiNi-L})]^{2-} + L\). Note that the Ni–L fragment does not provide cluster-bonding electrons and, therefore, \([\text{Ni}(@\text{Ge}_9\text{Ni-L})]^{2-}\) and \([\text{Ni}(@\text{Ge}_9)]^{2-}\) have the same number of such electrons, 20, despite the different numbers of vertices. This situation makes \([\text{Ni}(@\text{Ge}_9\text{Ni-L})]^{2-}\), as well as each half of \(I\), hypo-electronic because a deltahedron with 10 vertices should have \(2n + 2 = 22 (n = 10)\) cluster-bonding electrons according to Wade’s rules. The reason for the deviation is clearly the shape of the cluster which differs greatly from the shape expected for a 10-atom deltahedron (a bicapped square antiprism). The same unusual shape and electron count was also observed for 10-atom indium clusters centered by \(\text{Ni}, \text{Pd}, \text{or Pt}, [\text{M}(\text{In})_n]^{10-}\). The relation between the shape and the electron count was explained in molecular orbital terms for these clusters. In short, the central \(d^{10}\) atom does not bring additional cluster-bonding electrons but provides central orbitals for overlap with the cluster orbitals and, therefore, improves the bonding within the cluster. A nine-atom deltahedron with the shape of a tricapped trigonal prism (20 cluster-bonding electrons) has a LUMO that is bonding within the triangular bases of the prism but is antibonding between them. Therefore, elongation of the prismatic edges (those between the triangular bases) reduces the antibonding character of the orbital while opening of a triangular base reduces its bonding character. Thus, the position of this orbital, and therefore its occupancy, depends very strongly on which of these distortions prevails in each particular case. Note that the addition of a tenth vertex along the threefold axis of the prism to cap one of the bases does not change the electronic requirements. The orbital in question is empty for \([\text{M}(\text{In})_n]^{10-}\), \([\text{Ni}(@\text{Ge}_9\text{Ni-L})]^{2-}\), and the two halves of 1, while it is occupied by a single electron in \([\text{Ni}(@\text{Ge}_9)]^{2-}\) (and many examples of \([\text{Ge}_9]\)). Furthermore, as for empty nine-atom germanium clusters, centered clusters with different charges may be in equilibria between themselves and solvated electrons. This situation would provide \([\text{Ni}(@\text{Ge}_9)]^{2-}\) ions in the solution in addition to \([\text{Ni}(@\text{Ge}_9)]^{2-}\). The new ions \([\text{Ni}(@\text{Ge}_9)\text{Ni}(@\text{Ge}_9)]^{2+}\) are intact in solution, that is, they do not form simply upon crystallization. This was demonstrated by electrospray mass spectroscopy of a dimethylformamide (DMF) solution of \([K(@2,2,2\text{-crypt})]_2-\) \([\text{Ni}(@\text{Ge}_9)]\) 2.0 M. The spectrum, acquired in negative-ion mode, shows clearly the signal for the dianion \([\text{Ni}(@\text{Ge}_9)]^{2-}\) with an isotope distribution matching perfectly the calculated one (Figure 3). The new compound is EPR silent (crystalline sample at room temperature), which indicates that the nickel centers have a \(d^{10}\), \(d^{10}\) configuration.
Experimental Section

All manipulations were carried out under an inert atmosphere using standard Schlenk-line and glovebox techniques. Ethylenediamine (Acros, 99%) was distilled over sodium metal, collected and redistilled over K₄Sn₉ and/or K₄Pb₉ intermetallics. The K₄Ge₉ (Acros, 99%) was distilled over sodium metal, collected and layered with toluene, and left undisturbed to allow for desolvation. The resulting dark red–brown solution was filtered. The filtrate was layered with toluene and left undisturbed. It yielded a bright red solution. K₄Ge₉ (78 mg, 0.096 mmol) and [Ni(cod)₂] (64 mg, 0.232 mmol) were dissolved in ethylenediamine (2 mL) yielding a bright red solution. [Ni(cod)₂] (117 mg, 0.310 mmol) were dissolved in ethylenediamine (2 mL) in a test tube inside a glovebox yielding an intensely red solution. [Ni(cod)₂] (82 mg, 0.298 mmol) was added to this solution, and the mixture was allowed to stir for 3 h yielding a dark reddish brown suspension. The suspension was filtered, and the resulting dark brown filtrate was layered with toluene and left undisturbed. The resulting dark brown solution was filtered. The filtrate was collected and layered with toluene, and the mixture was allowed to stir for 2 h. The resulting solution afforded large bright red blocks of [K(2,2,2-crypt)]₄[Ni₃@Ge₉]₂·tol. Data sets were collected on a Bruker APEX diffractometer with a cold stream of the diffractometer. The crystals were selected under Paratone-N oil, mounted on fibers, and positioned in selected under Paratone-N oil, mounted on fibers, and positioned in Paratone-N oil. The structures were solved and refined (on F²) with the aid of the SHELXTL5.1 package. Crystal data for [K(2,2,2-crypt)]₄[Ni₃@Ge₉]₂·tol: monoclinic, P2₁/n, a = 14.439(2), b = 28.830(4), and c = 16.563(2) Å, β = 115.716(3)°, V = 6211.9(1) Å³, R₁ = 0.0932 for the observed data. CCDC-263116 for [K(2,2,2-crypt)]₄[Ni₃@Ge₉]₂·tol and CCDC-263117 for [K(2,2,2-crypt)]₆[Ni@Ge₉]₂·3en contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: February 17, 2005
Revised: April 7, 2005
Published online: June 1, 2005

Keywords: cluster compounds · germanium · nickel · zintl anions