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Synthesis and Isolation of $[Fe@Ge_{10}]^{3-}$: A Pentagonal Prismatic Zintl Ion Cage Encapsulating an Interstitial Iron Atom

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Reaction of an ethylenediamine (en) solution of the Zintl phase precursor K_4Ge_9 with $FeAr_2$ (Ar = 2,6-$Mes_2C_6H_3$)[1] in the presence of 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) yielded the endohedral Zintl ion $[Fe@Ge_{10}]^{3-}$ (**1**, Figure 1) which was crystallographically characterized as a $[K(2,2,2\text{-crypt})]^+$ salt in $[K(2,2,2\text{-crypt})]_3[Fe@Ge_{10}]$•2en.[2,3] This unprecedented Zintl ion exhibits a pentagonal prismatic 10-atom germanium cage with an interstitial iron atom in the central cavity. The pseudo D_{5h} geometry of the cluster and the coordination environment of the focal metal atom are reminiscent of the eclipsed isomer of ferrocene or Ellis' $[Ti(\eta^5\text{-}P_5)_2]^{2-}$ anion;[4] however notable differences in bonding and structure set **1** apart.

The reaction to yield **1** proceeds *via* the reductive cleavage of the two Fe−C bonds of the homoleptic organometallic reagent by the solvated electrons present in ethylenediamine solutions of K_4Ge_9.[5] Reductive M−C bond activation of post-transition metal organometallic reagents such as $M(C_6H_5)_2$ (M = Zn, Hg) and $Cu_5(Mes)_5$ (Mes = 2,4,6-$Me_3C_6H_2$) has recently been employed in the field of Zintl ion chemistry to give rise to a variety of novel functionalized and endohedral Zintl ions.[6] Extension of such studies to analogous transition metal organometallics seemed a viable route toward transition metal functionalized cluster anions; however despite the wealth of research in the area the number of monomeric low-coordinate transition metal aryl complexes is still relatively small.[1,7] One such species, the two-coordinate $FeAr_2$, proved ideally suited for our purposes. Similarly to what has been previously reported for post-transition metal organometallics such as $Zn(C_6H_5)_2$,[6a] reductive cleavage of an M−Ar bond would give rise to the Ar^- anion, which *via* a solvolysis reaction with the en solvent, would yield ArH and an amide. The reaction proceeds nonstoichiometrically, giving rise to a cluster of higher nuclearity than that of the precursor, $[Ge_9]^{n-}$ ($n = 2-4$), implying that a certain degree of cluster decomposition must take place to yield **1**. Furthermore, $[K(2,2,2\text{-crypt})]_3$**1**•2en was found to crystallize alongside unreacted nine-atom Ge Zintl ions such as $[Ge_9]^{3-}$ and $[Ge_9-Ge_9]^{6-}$ making the isolation of a compositionally pure solid sample unviable.

The pentagonal prismatic geometry exhibited by **1** is remarkable for a substituent-free group 14 cluster. An example of a related organically functionalized "empty" cluster can be found in the neutral [5]prismane $[SnR]_5$ (R = 2,6-$Et_2C_6H_3$), an electron precise "three-connect" cluster.[8] Similar prismanes of the majority of the group 14 elements (Si−Sn) have been relatively well-documented in the literature and exhibit two-center two-electron bonds for each of the contacts in the prismatic cluster frameworks.[9] However all of these species have organic functionalities bound to the cluster atoms, and no known substituent-free prismanes have been isolated to date.[10]

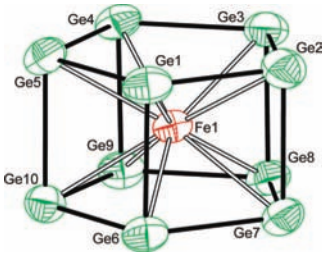

Figure 1. Thermal ellipsoid plot of $[Fe@Ge_{10}]^{3-}$. Anisotropic displacement ellipsoids pictured at 50% occupancy. Interatomic distances (Å): Ge1−Ge2, 2.5319(8); Ge1−Ge5, 2.5374(7); Ge1−Ge6, 2.6222(6); Ge2−Ge3, 2.5462(8); Ge2−Ge7, 2.6049(7); Ge3−Ge4, 2.5418(7); Ge3−Ge8, 2.6065(6); Ge4−Ge5, 2.5299(6); Ge4−Ge9, 2.6092(6); Ge5−Ge10, 2.6091(6); Ge6−Ge10, 2.5259(7); Ge6−Ge7, 2.5438(7); Ge7−Ge8, 2.5304(7); Ge8−Ge9, 2.5306(7); Ge9−Ge10, 2.5301(6); Fe1−Ge, 2.5087(7)−2.5353(7).

Cluster **1** is a unique endohedral cluster. All of the "naked" endohedral Zintl ions isolated to date fall under the category of electron-deficient deltahedral clusters. Species such as $[Cu@E_9]^{3-}$ (E = Sn, Pb),[6c] $[Ni@Pb_{10}]^{2-}$,[11] $[M@Pb_{12}]^{2-}$ (M = Ni, Pd, Pt),[12] $[M_2Sn_{17}]^{4-}$ (M = Ni, Pt),[13] $[Ni(Ni@Ge_9)_2]^{4-}$,[14] and $[Pd_2@E_{18}]^{4-}$ (E = Ge, Sn)[15,16] all exhibit deltahedral structures. Furthermore, such clusters have an insufficient number of electrons for two-center two-electron bonding. Subsequently their electronic structures can only be rationalized by employing Wade/Mingos rules for bonding in electron-deficient clusters.[17]

Interatomic cluster distances in **1** vary between 2.5259(7) and 2.6222(6) Å and are of a comparable magnitude to those observed in prismanes such as $[(Me_3Si)_2CHGe]_6$ (2.516(6)−2.584(6) Å).[9a] The five longest distances correspond to those linking the pentagonal faces of the prism, which range between 2.6049(7) and 2.6222(6) Å. These are 0.06−0.1 Å longer than the interatomic distances of the pentagonal faces which were found to vary narrowly between 2.5259(7) and 2.5462(7) Å. Interatomic distances between the interstitial Fe atom and the Ge atoms of the cluster cage vary between 2.5087(7) and 2.5353(7) Å. These distances are longer than any Fe−Ge bond distances reported to date, the longest of which (2.497(1) Å) was observed for $[CpFe(CO)_2]_2Ge(N^tBu)_2SiMe_2$.[18] This is indicative of the relatively weak bonding effects between the interstitial atom and the cluster cage. Bond angles between prismatic edges and pentagonal faces are all close to 90° varying between 88.90(2)° and 91.04(2)°.

The geometry exhibited by **1** poses several questions about the electronic structure of this unusual anion. Both geometry and electron count indicate that the cluster does not follow conventional rules for bonding in deltahedral clusters.[17] The 10 Ge atoms should

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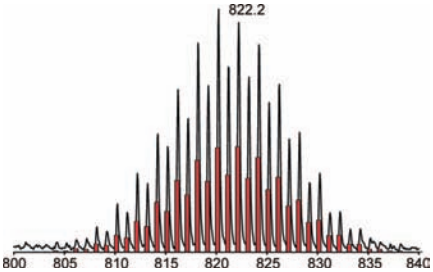

Figure 2. Negative ion-mode electrospray mass envelope corresponding to $\{K^+[Fe@Ge_{10}]^{2-}\}^-$. Recorded experimental data are given in black with the calculated isotopic distribution in red.

each contribute two electrons for cluster bonding, assuming each atom has a lone pair of electrons pointing radically outward from the cluster. These 20 electrons in addition to the 3 electrons from the overall cluster charge and the 8 provided by the interstitial iron equals a total of 31 e^- for cluster bonding (indicating that cluster **1** should be paramagnetic). A deltahedral cluster missing seven vertices would require 36 e^- according to Wade's rules. Alternatively, a three-connect pentagonal prismane will need a total of 30 electrons to form 15 two-center, two-electron bonds; however this does not take into account the presence of an interstitial atom. Interestingly, theoretical studies on related endohedral clusters $[M@Ge_{10}]^{2-}$ (M = Pd, Pt) have found that a pentagonal prismatic geometry is favored, yet until now no such species had been observed.[19]

Confirmation of the presence of the cluster anion in solution was obtained by electrospray mass spectrometry of DMF solutions of the crystalline product from which [K(2,2,2-crypt)]$_3$**1**•2en was isolated. All peaks appear as distinct mass envelopes due to the multiple Ge isotopes, which allows for the unequivocal assignment of cluster-based signals. As is often the case with the negative ion-mode electrospray mass spectra of anionic Zintl ions, the clusters are observed with reduced charges as a result of the oxidation of the parent clusters during the ionization process. Furthermore, there is also evidence of extensive ion pairing between anions and charge balancing cations. Subsequently, the negative ion mode spectrum of **1** revealed mass envelopes corresponding to $[Fe@Ge_{10}]^-$ (m/z = 781.2), $\{K^+[Fe@Ge_{10}]^{2-}\}^-$ (m/z = 822.2, Figure 2), and $\{[K(2,2,2\text{-crypt})]^+[Fe@Ge_{10}]^{2-}\}^-$ (m/z = 1198.7) peaks. The positive ion mode spectrum of cluster **1** revealed a peak corresponding to the $\{[K(2,2,2\text{-crypt})]_4[Fe@Ge_{10}]^{3-}\}^+$ ion pair at m/z = 2443.9. Due to the nonstoichiometric nature of the reaction by which **1** was synthesized, mass spectrometry also revealed the presence of the nine-atom Ge precursor.

At present we are conducting several studies into synthesizing analytically pure solid samples of **1** and related complexes with the aim of investigating their physical properties (magnetism, spectroscopy, etc.).

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Supporting Information Available: X-ray crystallographic file in CIF format.This material is available free of charge via the Internet at http://pubs.acs.org.

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(2) All operations were carried out under an inert atmosphere employing standard Schlenk-line or glovebox techniques. Ethylenediamine (99%, Aldrich) was distilled over sodium metal while toluene (99.9%. Rathburn Chemicals, Ltd.) and THF (99.9%. Rathburn Chemicals, Ltd.) were purified through an MBraun MB SPS-800 solvent system. All solvents were stored in gas-tight ampoules under argon. The intermetallic precursor, K_4Ge_9, was synthesized from a stoichiometric mixture of the elements (K: 99.95%, Aldrich; Ge: 99.999% Strem) according to a previously reported synthetic procedure. [K(2,2,2-crypt)]$_3$[Fe@Ge$_{10}$]•2en: K_4Ge_9 (62 mg, 0.077 mmol), FeAr$_2$ (26 mg, 0.038 mmol), and 2,2,2-crypt (50 mg, 0.133 mmol) were weighed out into a test tube inside a nitrogen-filled glovebox. The solids were dissolved in ethylenediamine (2 mL) and trace amounts of THF were added to aid in the dissolution of FeAr$_2$. The reaction mixture was allowed to stir for 1 h, yielding a dark brown solution which was subsequently filtered and layered with toluene to allow for crystallization. Small greenish black rodlike crystals of [K(2,2,2-crypt)]$_3$[Fe@Ge$_{10}$]•2en suitable for single-crystal X-ray diffraction were obtained after 3 days alongside crystals of other known $[Ge_9]^{n-}$ clusters. ES-MS: m/z 781.2 $[Fe@Ge_{10}]^-$, 822.2 $\{K[Fe@Ge_{10}]\}^-$, 1198.7 $\{[K(2,2,2\text{-crypt})][Fe@Ge_{10}]\}^-$. ES+ MS: m/z 2443.9 $\{[K(2,2,2\text{-crypt})]_4[Fe@Ge_{10}]\}^+$.

(3) Single crystal X-ray diffraction data were collected at 150 K on an Enraf-Nonius Kappa-CCD diffractometer equipped with an Oxford Cryosystems low-temperature device. The crystal was mounted on a glass fiber using N-Paratone oil and quickly placed under the nitrogen flow of the cryostream. Data were collected using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å); equivalent reflections were merged, and the images were processed with the DENZO and SCALEPACK programs. Corrections for Lorentz polarization effects and absorption were performed, and the structures were solved by direct methods using SIR92. The structures were refined on F^2 using SHELXL. Crystallographic data for [K(2,2,2-crypt)]$_3$[Fe@Ge$_{10}$]•2en: triclinic, $P\bar{1}$, a = 14.4014(1), b = 15.7227(1), c = 21.6608(2), α = 93.2587(3), β = 100.4043(3), γ = 107.2794(4), V = 4574.29(6), Z = 2, R1/wR2 4.38/11.88% for the observed data ($I \geq 2\sigma(I)$), R1/wR2 5.72, 12.56% for all the data.

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