Filled Trivacant Icosahedra as Building Fragments in 17-atomic Endohedral Germanides [TM_2@Ge_{17}]$^{n-}$ (TM = Co, Ni)

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Supporting information

1. Experimental details

General

All experiments were carried out under oxygen-free, dry conditions using standard glove box and Schlenk line techniques. Glassware was dried prior to use by heating it *in vacuo*. The solid-state phase K_4Ge_9 is prepared by fusion of stoichiometric amounts of the elements in a stainless-steel autoclave at 650 °C. The phase of nominal composition "$K_5Co_{1.2}Ge_9$"[1] and the titanyl complex $[Cp_2Ti(NH_3)_2]Cl(NH_3)$[2] are prepared according to the literature. $Ni(cod)_2$ (*Sigma Aldrich*, stored at -30 °C under Ar) is used without further purification. Liquid ammonia was dried over sodium metal, and [2.2.2]crypt (*Merck*) was dried overnight applying dynamic vacuum before usage. Ethylenediamine (en) was dried over CaH_2 at 120 °C for two days prior to distillation, toluene was obtained from an MBraun Grubbs apparatus and stored over molecular sieve.

ESI MS analysis

ESI MS analyses were performed on a Bruker Daltronic HCT mass spectrometer (dry gas temperature: 300 °C; injection speed: 300 µL/h), and the data evaluation was carried out using the Bruker Compass Data Analysis 4.0 SP 5 program (Bruker). Spectra were plotted using OriginPro2016G (Origin Lab) and Excel 2016 (Microsoft).

EDX analysis

EDX measurements were performed using a Hitachi TM-1000 tabletop spectroscope. Data evaluation was performed using the SWIFT-ED-TM program (Oxford Instruments).

Single crystal structure determination

Air- and moisture-sensitive crystals of **1** and **3** were transferred from the mother liquor into cooled perfluoroalkyl ether oil and isolated from polycrystalline material under a cooled stream of nitrogen.[3] Crystals of **2** were selected under a microscope in the glove box. For diffraction data collection, the single crystals were mounted on a glass capillary and positioned in a 150 K cold N_2 gas stream. Data collection was performed with a STOE StadiVari diffractometer (Mo *Kα* radiation) equipped with a DECTRIS PILATUS 300K detector. Structures were solved by Direct Methods (SHELXS-97) and refined by full-matrix least-squares calculations against F^2 (SHELXL-2014 or SHELXL-2018).[4] The hydrogen atoms were positioned in calculated positions and refined using a riding model. Unless stated otherwise, all non-hydrogen atoms were treated with anisotropic displacement parameters. Cluster volumes were calculated using VESTA.[5] Further details of the crystal structure investigations may be obtained from the joint CCDC/FIZ Karlsruhe online deposition service: https://www.ccdc.cam.ac.uk/structures/? by quoting the depository numbers CCDC-2081217 (**1**), CCDC-2081218 (**2**), and CCDC-2081219 (**3**). The crystallographic data for compounds **1** - **3** are summarized in Table S1.

Quantum chemical calculations

Quantum chemical calculations were performed with the TURBOMOLE program package,[6] using the PBE0 hybrid density functional method[7, 8] and polarized triple-ζ-valence Karlsruhe basis sets (DFT-PBE0/TZVP with def2-TZVP on Ge and Ni/Co).[9] Multipole-accelerated resolution-of-the-identity technique was used to speed up the calculations.[10-12] $m4$ integration grid was applied for the numerical integration of the exchange-correlation functional. As initial structures the data of the crystal structure determinations of compounds **1a** and **2a** were used. The structures were optimized without any symmetry constraints. A COSMO solvent field was applied to counter the anionic charge.[13]

Synthesis of compounds 1 – 3

[K([2.2.2]crypt)]$_2$K$_4$[Co$_2$@Ge$_{17}$] · 15 NH$_3$ (1)

"K$_5$Co$_{1.2}$Ge$_9$" (100 mg, 0.113 mmol, 1 equiv.), [Cp$_2$Ti(NH$_3$)$_2$]Cl(NH$_3$) (28 mg, 0.113 mmol, 1 equiv.) and [2.2.2]crypt (76.8 mg, 0.204 mmol, 1.8 equiv.) were weighed into a Schlenk tube. Subsequently liquid ammonia (5 mL) was condensed onto the solid mixture leading to the formation of a deep red solution. A black crystal suitable for single crystal X-ray diffraction could be isolated after 6 months.

[K([2.2.2]crypt)]$_4$[Ni$_2$@Ge$_{17}$] · en (2)

The synthesis generally followed the method applied by *Sevov* and co-workers for the synthesis of the cluster unit [Ni$_3$@Ge$_{18}$]$^{4-}$.[14]

K$_4$Ge$_9$ (121.6 mg, 150.1 mmol, 1 equiv.), Ni(cod)$_2$ (90.8 mg, 330.1 mmol 2.2 equiv.) and [2.2.2]crypt (169.4 mg, 450.0 mmol, 3 equiv.) were weighted into a Schlenk tube, and en (2.5 mL) was added via a syringe. After stirring the reaction for 2 h, the dark suspension was filtered over a glass filter-packed pipette, and the resulting filtrate was carefully layered with toluene (2 mL). After two month of crystallization time, small amounts of brown, block-shaped single crystals were collected (crystalline yield approximately 5 % based on the [Ge$_9$] precursor).

ESI MS: *m/z* 1352.5 for [Ni$_2$@Ge$_{17}$]$^-$ and *m/z* 1767.8 for [K([2.2.2]crypt)][Ni$_2$@Ge$_{17}$]$^-$. **EDX:** K, Ni, Ge (qualitative).

[K(2.2.2-crypt)]$_3$[Co@Ge$_{10}$] · 9 NH$_3$ (3)

A black crystal of **3** suitable for single crystal X-ray diffraction was isolated after 5 months from the same reaction solution from which [K([2.2.2]crypt)]$_2$K$_4$[Co$_2$@Ge$_{17}$] · 15 NH$_3$ (**1**) was isolated one month later. Since crystals can only be isolated from liquid ammonia one after another it is not entirely clear if the 10-atom cluster formed simultaneously with anion **1a** or if **1a** formed due to opening the reaction flask.

2. Crystallographic details

Table S1. Crystallographic data of compounds **1** – **3**.

Compound	**1**	**2**	**3**
formula	$K_6N_{19}O_{12}C_{36}H_{117}Co_2Ge_{17}$	$K_4N_{10}O_{24}C_{74}H_{152}Ni_2Ge_{17}$	$K_3N_{15}O_{18}C_{54}H_{134}CoGe_{10}$
fw / g·mol^{-1}	2594.97	3073.9	2184.89
space group	$P2_1/c$	$C2/c$	$P\bar{1}$
a / Å	19.6865(6)	27.8606(5)	12.414(2)
b / Å	32.1696(10)	16.5164(2)	16.140(2)
c / Å	15.3982(4)	27.9518(4)	25.212(3)
α / deg	90	90	72.851(9)
β / deg	110.634(2)	117.468(1)	89.887(9)
γ / deg	90	90	70.505(9)
V / Å^3	9126.2(5)	11412.2(3)	4524.1(9)
Z	4	4	2
T / K	150	150(2)	150(2)
λ / Å	0.71073	0.71073	0.71073
ρ_{calcd} /g·cm^{-3}	1.889	1.789	1.604
μ /mm^{-1}	6.181	4.932	3.649
collected reflections	277912	155284	15796
indep. reflections	17914	11191	13148
R_{int} / R_δ	0.1763/0.0555	0.0487/0.0183	0.0965/0.1500
parameters / restraints	834/6	614/19	910/104
R_1 [$I > 2\,\sigma(I)$ / all data]	0.0472/0.0683	0.0714/0.0873	0.0757/ 0.1618
wR_2 [$I > 2\,\sigma(I)$ / all data]	0.1053/0.1142	0.1525/0.1648	0.1682/0.2110
goodness of fit	1.028	1.071	0.902
max./min. diff. el. density / e·Å^{-3}	1.553/-1.455	4.568/-3.875	1.280/-1.651
CCDC	2081217	2081218	2081219

[K([2.2.2]crypt)]₂K₄[Co₂@Ge₁₇] · 15 NH₃ (1)

Table S2. Selected interatomic distances and angles in anion **1a**.

Atoms	distance / Å	atoms	distance / Å
Ge1-Ge2	2.6374(9)	Ge1-Co1	2.4317(9)
Ge1-Ge3	2.8083(9)	Ge2-Co1	2.4421(9)
Ge1-Ge4	2.6244(9)	Ge3-Co1	2.4618(9)
Ge1-Ge5	2.9199(9)	Ge4-Co1	2.4484(9)
Ge1-Ge6	2.8851(9)	Ge5-Co1	2.4021(10)
Ge2-Ge3	2.6682(9)	Ge6-Co1	2.3940(9)
Ge2-Ge6	2.7221(9)	Ge7-Co1	2.4167(10)
Ge2-Ge7	2.6768(9)	Ge8-Co1	2.3934(9)
Ge3-Ge4	2.6963(10)	Ge9-Co1	2.1924(9)
Ge3-Ge7	2.7359(9)	Ge9-Co2	2.1998(9)
Ge3-Ge8	2.7664(10)	Ge10-Co2	2.3927(10)
Ge4-Ge5	2.7229(9)	Ge11-Co2	2.4041(9)
Ge4-Ge8	2.6719(10)	Ge12-Co2	2.4184(10)
Ge5-Ge6	2.6099(9)	Ge13-Co2	2.3932(9)
Ge5 Ge9	2.9316(9)	Ge14-Co2	2.4528(10)
Ge6-Ge9	2.8983(9)	Ge15-Co2	2.4481(9)
Ge7-Ge8	2.6264(9)	Ge16-Co2	2.4412(9)
Ge7-Ge9	2.9589(9)	Ge17-Co2	2.4385(10)
Ge8-Ge9	2.9763(9)		
Ge9-Ge10	2.9301(9)		
Ge9-Ge11	2.9376(9)		
Ge9-Ge12	2.9303(9)		
Ge9-Ge13	2.9056(9)		
Ge10-Ge11	2.6510(9)		
Ge10-Ge14	2.7027(9)		
Ge10-Ge15	2.7903(9)		
Ge11-Ge17	2.6637(9)		
Ge12-Ge13	2.6061(9)	**atoms**	**angle / deg**
Ge12-Ge17	2.6638(9)	Co1-Ge9-Co2	166.9(1)
Ge13-Ge14	2.7351(10)		
Ge13-Ge16	2.8129(9)		
Ge14-Ge15	2.6567(10)		
Ge14-Ge16	2.6609(10)		
Ge15-Ge16	2.7542(9)		
Ge15-Ge17	2.7170(10)		
Ge16-Ge17	2.6751(9)		

[K([2.2.2]crypt)]₄[Ni₂@Ge₁₇] · en (2)

Atoms Ge5, C38 and N6 were refined using an ISOR (0.01) command; the distance between C38 and N6 was restrained with a DFIX (1.5) command.

The high maximum and minimum difference electron density is mainly located in close distance around Ge5 indicating a more complex disorder than described by the present refinement. However, a refinement with the Ge5 atom at more than the given split positions was not successful. A refinement with other elements than Ge (e.g. Ni) on position Ge5 resulted in worse reliability factors.

Table S3. Selected interatomic distances and angles in **2a**. Symmetry operation (i): 1-x, y, 0.5-z.

| atoms	distance / Å	atoms	distance / Å
Ge1-Ge2	2.683(1)	Ge1-Ni1	2.433(1)
Ge1-Ge2^i	2.676(1)	Ge2-Ni1	2.462(1)
Ge1-Ge3	2.869(1)	Ge3-Ni1	2.411(1)
Ge1-Ge4	2.825(1)	Ge4-Ni1	2.422(1)
Ge1-Ge1^i	2.713 (2)	Ge5-Ni1	2.236(3)
Ge1-Ge2^i	2.676(1)	Ge5-Ni2	2.144(3)
Ge1^i-Ge2	2.676(1)	Ge6-Ni2	2.390(1)
Ge1^i-Ge2^i	2.683(1)	Ge7-Ni2	2.390(1)
Ge1^i-Ge3^i	2.869(1)	Ge8-Ni2	2.435(1)
Ge1^i-Ge4^i	2.825(1)	Ge9-Ni2	2.394(1)
Ge2-Ge3	2.667(1)	Ni1-Ni2	4.215(2)
Ge2-Ge4^i	2.725(1)		
Ge2^i-Ge4	2.725(1)		
Ge2^i-Ge3^i	2.667(1)		
Ge3-Ge4	2.622(1)		
Ge3-Ge5^i	2.735(5)		
Ge3^i-Ge5	2.735(5)		
Ge3^i-Ge4^i	2.622(1)		
Ge4-Ge5^i	2.501(4)		
Ge4^i-Ge5	2.501(4)		
Ge5-Ge7	2.415(4)		
Ge5-Ge6^i	2.799(6)		
Ge5i-Ge6	2.903(6)		
Ge5^i-Ge7^i	2.411(4)		
Ge6-Ge7	2.589(1)		
Ge6-Ge8	2.657(1)	**atoms**	**angle / deg**
Ge6-Ge9	2.896(1)	Ni1-Ge5-Ni2	148.4(1)
Ge6^i-Ge7^i	2.589(1)	Ni1-Ge5^i-Ni2	148.4(1)
Ge6^i-Ge8^i	2.657(1)		
Ge6^i-Ge9^i	2.896(1)		
Ge7-Ge8^i	2.706(2)		
Ge7^i-Ge8	2.706(2)		
Ge7^i-Ge9^i	2.833(2)		
Ge8-Ge9	2.696(2)		
Ge8-Ge9^i	2.681(1)		
Ge8^i-Ge9	2.681(1)		
Ge8^i-Ge9^i	2.696(2)		
Ge9-Ge9^i	2.704(2)		
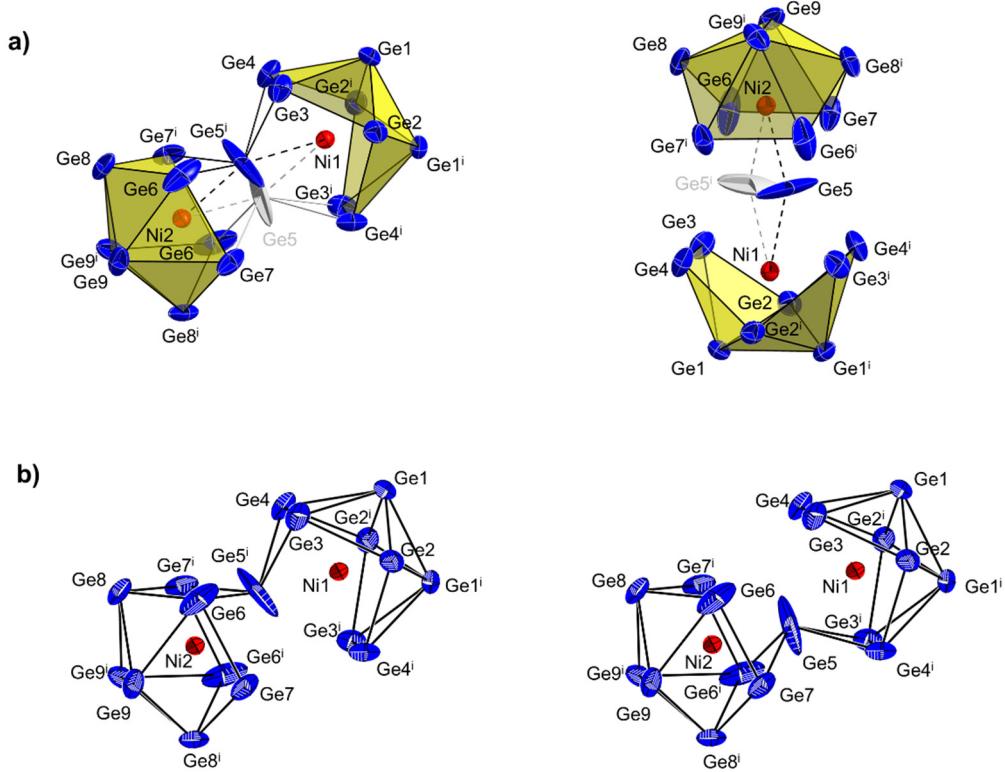
Figure S1. Different views of anion **2a**. a) Emphasis on the [Ge$_8$] tubs forming the cluster and representation of the split position of Ge5 (site occupation factor of 0.5 each). b) Structure of anion **2a** emphasizing the single split positions. All atoms are represented with anisotropic displacement parameters at a 50 % probability level. Symmetry operation (i): 1-*x*, *y*, 0.5-*z*.

The novel cluster **2a** and the reported anion $[Ni_3@Ge_{18}]^{4-}$ [14] show building principles similar to a C_{4v} symmetric $[Ge_9]$ cluster (Figure S2).[15] However, the vertex atoms are dislocated from their original positions, which is caused by the incorporated Ni atoms resulting in elongated Ge-Ge distances. The longest distance between Ge atoms in the bare $[Ge_9]$ cage (characterized from solid state) can be found between $Ge5^A$-$Ge6^A$ with 2.88 Å[15] which is significantly shorter than the distances $Ge6^i$-$Ge7$ (3.89 Å) in $[Ni_2@Ge_{17}]^{4-}$ or $Ge5^B$-$Ge6^B$ (3.66 Å) in $[Ni_3@Ge_{18}]^{4-}$.[15] Figure S2 gives a comparison of the different structural motifs. The most prominent difference between $[Ge_9]^{4-}$, **2a** and $[Ni_3@Ge_{18}]^{4-}$ is that in the latter ion one Ge atom (drawn in yellow) is tilted out of the former pseudo square plane. This observation can be evaluated by measuring the dihedral angles of the plane which are $\omega_{Ge1A\text{-}Ge2A\text{-}Ge3A\text{-}Ge4A} = 1.8°$ ($[Ge_9]^{4-}$); $\omega_{Ge5i\text{-}Ge7i\text{-}Ge6\text{-}Ge8} = 1.7°$ (**2a**); $\omega_{Ge1B\text{-}Ge2B\text{-}Ge3B\text{-}Ge4B} = 44.0°$ ($[Ni_3@Ge_{18}]^{4-}$).
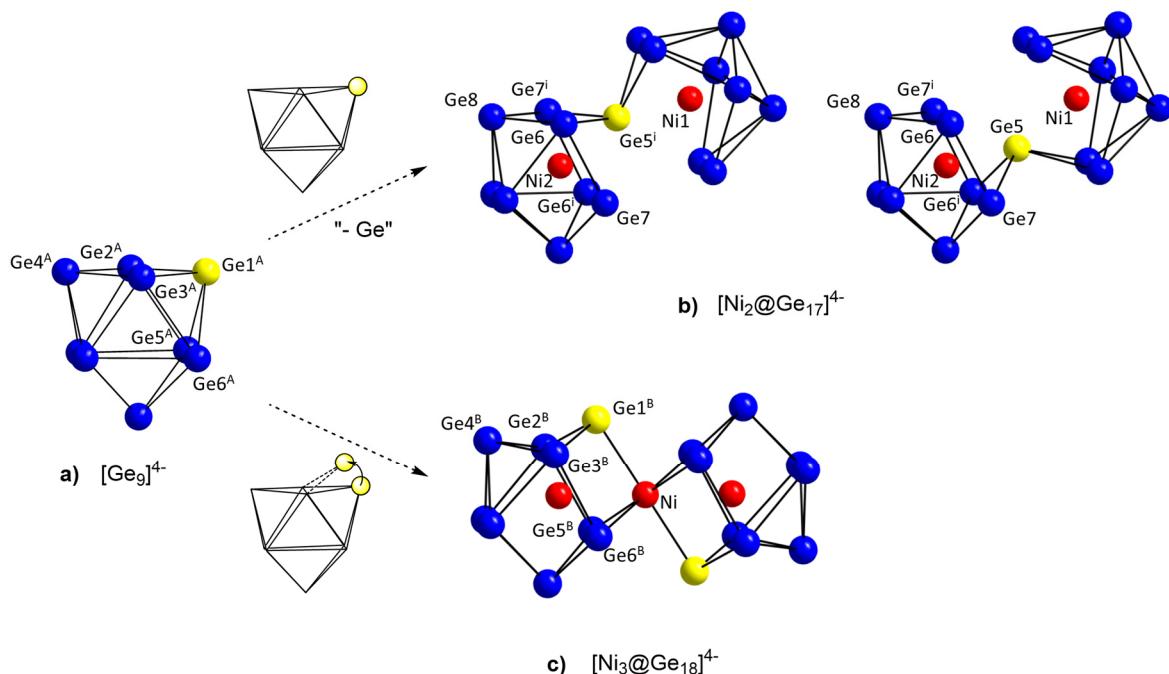
**Figure S2.** Representation of structural similarities and differences between a) $[Ge_9]^{4-}$,[15] b) the novel cluster **2a** ($[Ni_2@Ge_{17}]^{4-}$) and c) the known anion $[Ni_3@Ge_{18}]^{4-}$ [14] with respect to the position of one vertex atom (with yellow color) of the pseudo square plane in $[Ge_9]$. Symmetry operation (i): 1-x, y, 0.5-z.

Table S4. Summary of interatomic distances, angles and cluster volumes in the anions **1a** and **2a** in comparison to literature data.

	d(E–E) / Å	d(TM–E) / Å	∢ (TM–E–TM) / deg	dihedral angle of rectangular planes / deg	volume / Å^3
1a [Co$_2$@Ge$_{17}$]$^{6-}$	2.606(1) – 2.938(1)	2.192(1) – 2.462(1)	166.9(1)	14.0	26.68/ 26.82
1a optimized (K$_4$[Co$_2$@Ge$_{17}$]$^{2-}$)	2.631 – 2.938	2.184 – 2.446	168.9	11.7	26.35/ 26.34
2a [Ni$_2$@Ge$_{17}$]$^{4-}$	2.415(4) – 2.903(6)	2.144(3) – 2.462(1)	148.4(1)	0.0	26.71/ 25.86
2a optimized ([Ni$_2$@Ge$_{17}$]$^{4-}$)	2.567 – 2.938	2.205 – 2.461	146.5	14.7	26.75/ 26.69
[Co@Ge$_9$]$^{5-}$ [1]	2.683 – 2.811	2.331 – 2.374	–	–	26.40
[Ni@Ge$_9$]$^{3-}$ [16]	2.558 – 2.876	2.254 – 2.410	–	–	25.17/ 25.67
[Ni$_2$@Sn$_{17}$]$^{4-}$ [17]	2.971 – 3.209	2.382 – 2.740	180	0.0	–
[Rh$_2$@Sn$_{17}$]$^{6-}$ [18]	2.933 – 3.247	2.498 – 2.761	163.9	13.9	–

[K(2.2.2-crypt)]$_3$[Co@Ge$_{10}$] · 9 NH$_3$ (3)

Compound **3**, [K(2.2.2-crypt)]$_3$[Co@Ge$_{10}$] · 9 NH$_3$, was isolated from the same reaction solution anion **1a** has been obtained from before. The anion features the pentagonal prismatic ion [Co@Ge$_{10}$]$^{3-}$ (**3a**) which has been obtained previously from reactions in en solutions.[19, 20]
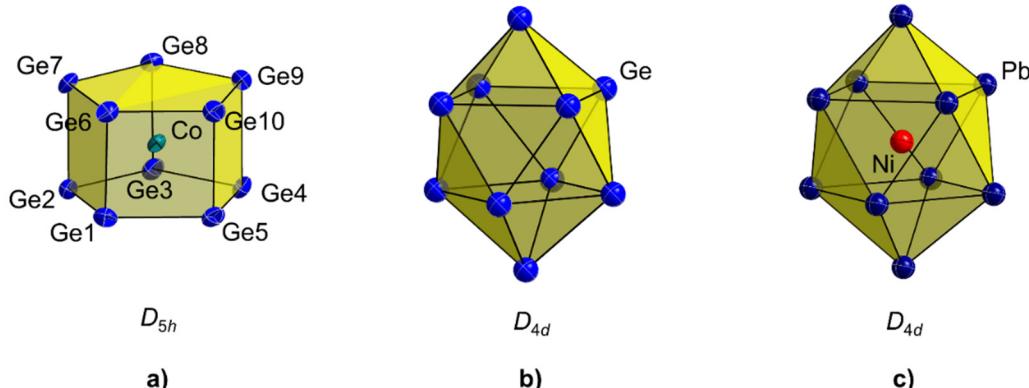

Figure S1. Structure of anion **3a** featuring D_{5h} symmetry. All ellipsoids are presented at a 50 % probability level. b) Structure of the anion [Ge$_{10}$]$^{2-}$ with D_{4d} symmetry.[21,22] c) Structure of the anion [Ni@Pb$_{10}$]$^{2-}$ with D_{4d} symmetry.[23]

The formation of a pentagonal prism for the Co-filled anion is rather unexpected, as both the empty [Ge$_{10}$]$^{2-}$ [21, 22] as well as the corresponding Ni-filled Pb[23] cluster feature deltahedral *closo*-clusters, i.e. doubly capped square antiprisms with D_{4d} symmetry (Figures S3b and c). Theoretical considerations revealed that a size effect has to be taken into account as a possible reason for the formation of the pentagonal prism around the larger Co$^-$ anion as compared to the smaller Ni^0 atoms or even unoccupied voids.[24] As the *h*/*e* ratio (*h*: height of prism; *e*: lengths of edges of the pentagonal surfaces) is close to 1, a polyhedron with D_{5h} symmetry results.

Table S5. Summary of interatomic distances in **3a**, the previously published [Co@Ge$_{10}$]$^{3-}$ anions[21] and the empty anion [Ge$_{10}$]$^{2-}$.[19,20]

	d(Ge–Ge)$_{edge}$ / Å	d(Ge–Ge)$_{height}$ / Å	d(Co–Ge) / Å	volume / Å	h_{max}/e_{min}	symmetry
3a [Co@Ge$_{10}$]$^{3-}$	2.501(2) – 2.538(2)	2.583(2) – 2.621(2)	2.494(2) – 2.516(2)	28.58	1.05	D_{5h}
[Co@Ge$_{10}$]$^{3-}$ [19]	2.502 – 2.527	2.600 – 2.622	2.479 – 2.525	28.55	1.05	D_{5h}
[Co@Ge$_{10}$]$^{3-}$ [20]	2.508 – 2.530	2.596 – 2.609	2.488 – 2.514	28.45	1.04	D_{5h}
[Ge$_{10}$]$^{2-}$ [21]	2.543 – 2.822	–	–	26.95	–	D_{4d}

Table S6. Selected interatomic distances in **3a**.

atoms	distance / Å	atoms	distance / Å
Ge1-Ge2	2.511(2)	Ge1-Co	2.511(2)
Ge1-Ge5	2.538(2)	Ge2-Co	2.503(2)
Ge1-Ge6	2.593(2)	Ge3-Co	2.494(2)
Ge2-Ge3	2.536(2)	Ge4-Co	2.501(2)
Ge2-Ge7	2.605(2)	Ge5-Co	2.512(2)
Ge3-Ge4	2.518(2)	Ge6-Co	2.509(2)
Ge3-Ge8	2.611(2)	Ge7-Co	2.516(2)
Ge4-Ge5	2.523(2)	Ge8-Co	2.512(2)
Ge4-Ge9	2.621(2)	Ge9-Co	2.507(2)
Ge5-Ge10	2.583(2)	Ge10-Co	2.512(2)
Ge6-Ge7	2.513(2)		
Ge6-Ge10	2.516(2)		
Ge7-Ge8	2.520(2)		
Ge8-Ge9	2.523(2)		
Ge9-Ge10	2.501(2)		

3. ESI MS sample preparation and spectra of 2a

ESI MS spectra of the reaction mixture were performed from (A) the solid precipitate and (B) the reaction solution after two months (Figure S4).

A: The supernatant solution was removed using a syringe, and the remaining dark precipitate was subsequently dissolved in dmf, filtered through a syringe filter and injected into the ESI MS.

B: An aliquot of the reaction solution (en) was diluted with dmf, filtered through a syringe filter and injected into the ESI MS.
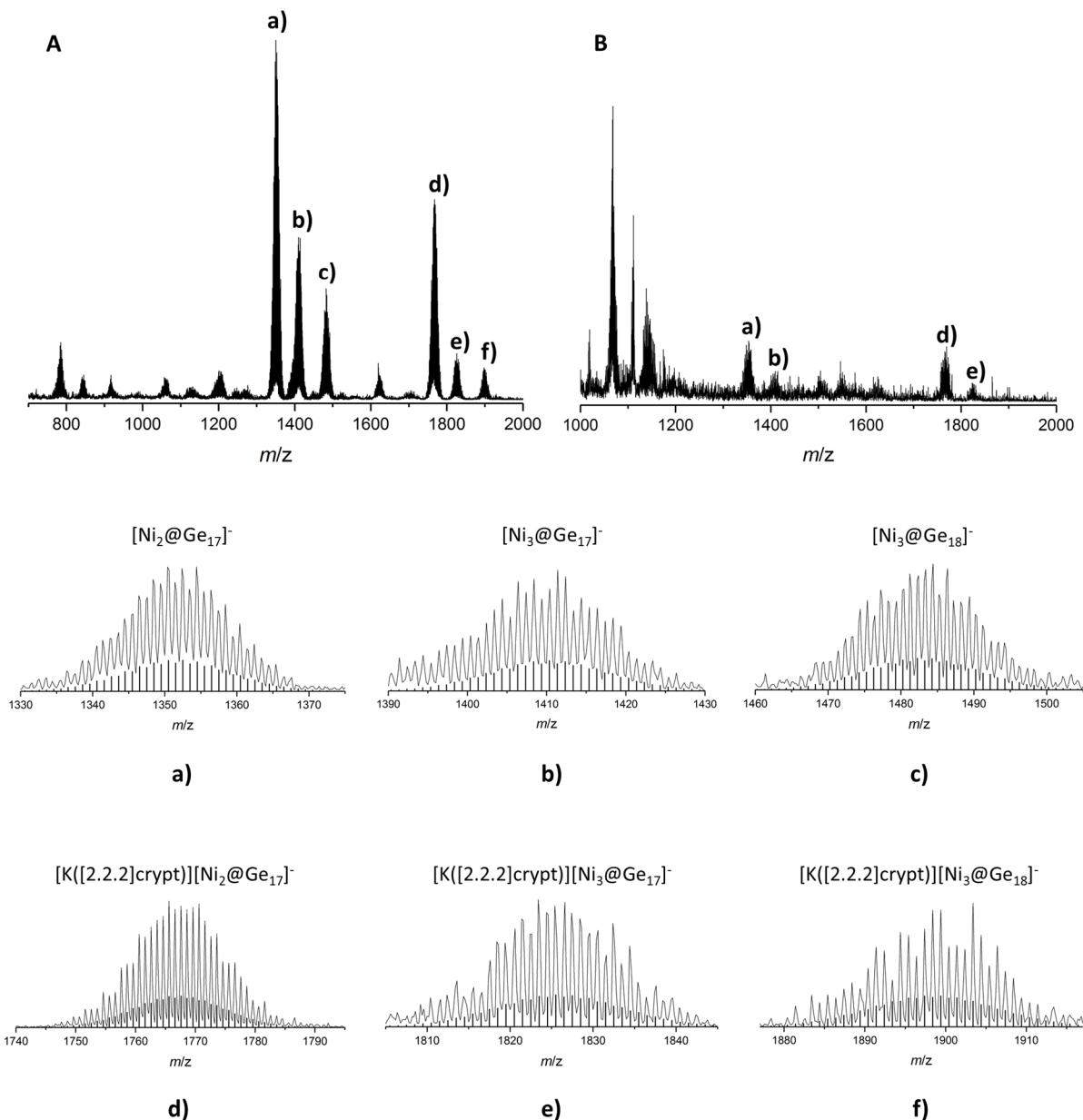
Figure S2. A: ESI MS spectrum of the precipitate of the reaction of K_4Ge_9, $Ni(cod)_2$ and [2.2.2]crypt recorded in dmf (negative ion mode, 2000V, 300 °C); B: ESI MS spectrum of the reaction solution of the reaction of K_4Ge_9, $Ni(cod)_2$ and [2.2.2]crypt recorded in dmf (negative ion mode, 2000V, 300 °C). The following molecule peaks are monitored: a) $[Ni_2@Ge_{17}]^-$ (*m/z* 1352.5), b) $[Ni_3@Ge_{17}]^-$ (*m/z* 1410.3), c) $[Ni_3@Ge_{18}]^-$ (*m/z* 1482.4), d) $[K([2.2.2]crypt)][Ni_2@Ge_{17}]^-$ (*m/z* 1767.8), e) $[K([2.2.2]crypt)][Ni_3@Ge_{17}]^-$ (*m/z* 1825.5), and f) $[K([2.2.2]crypt)][Ni_3@Ge_{18}]^-$ (*m/z* 1899.4). Calculated isotope patterns are presented as black bars.
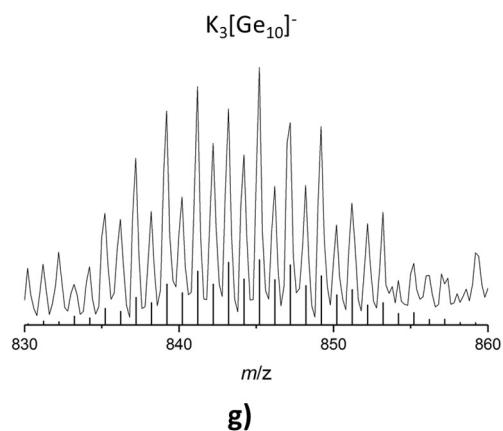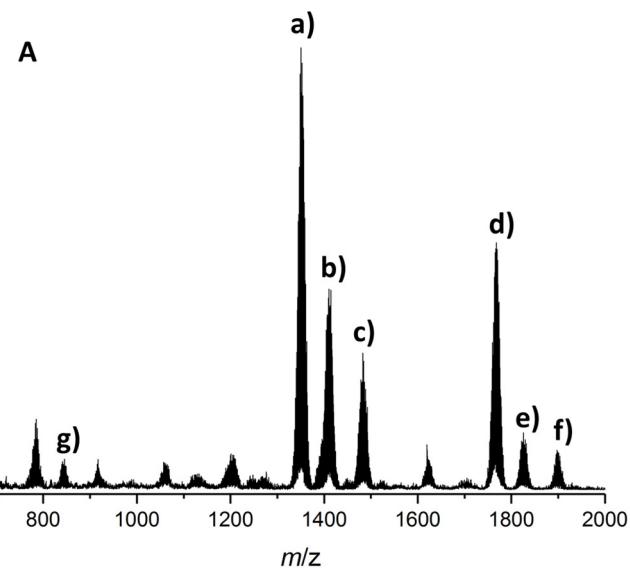
**Figure S5.** A: ESI MS spectrum of the precipitate of the reaction of K_4Ge_9, $Ni(cod)_2$ and [2.2.2]crypt recorded in dmf (negative ion mode, 2000V, 300 °C); a) - f) see Figure S4; g) $K_3[Ge_{10}]^-$ (*m/z* 843.1). Calculated isotope pattern is presented as black bars.

4. EDX analysis

Spectrum details

Project: CW-112.ipj
Spectrum name: Spectrum4

Acquisition conditions
Acquisition time (s) :   200.0   Process time :   4
Accelerating voltage (kV) :   15.0
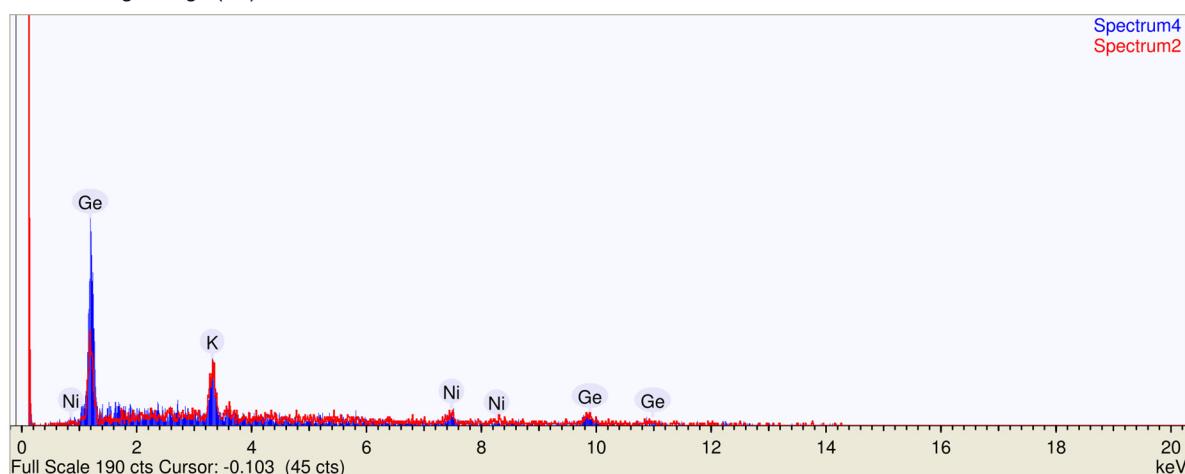
Figure S6. Qualitative EDX spectra of compound **2**. The red and blue lines resemble two point measurements at different crystal sites.

Single crystals of **2** were isolated from a heterogeneous/amorphous precipitate, thus hampering a quantitative EDX analysis. For compounds **1** and **3**, which were obtained from reactions in liquid ammonia, EDX measurements were not possible.

5. Computational details

Table S7. Summarized results of the structure optimization based on the single crystal diffraction data.

initial structure	optimized symmetry	total molecular energy / eV	HOMO-LUMO gap / eV	TM-Ge-TM (optimized) / deg	TM-Ge-TM (experimental) / deg	MO number	electrons (total)	lowest vibration frequency / cm^{-1}
$[Co_2@Ge_{17}]^{6-}$	s4	-1035966.5	2.95770	180.00	166.79	906	604	15.60
$K_4[Co_2@Ge_{17}]^{2-}$	d2d	-1101243.8	2.83937	168.86	166.79	1038	676	21.00
$[Ni_2@Ge_{17}]^{4-}$	c1	-1042795.9	2.85455	146.51	148.34	906	604	19.99

$[Co_2@Ge_{17}]^{6-}$
(DFT-optimized structure)
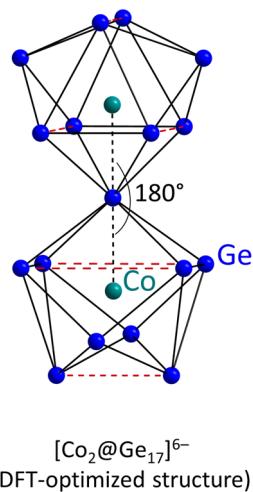
Figure S7. DFT-optimized structure of the anion $[Co_2@Ge_{17}]^{6-}$ with a linear arrangement of the strand Co-Ge-Co caused by the neglect of K$^+$ cations.

Additional DFT calculations were carried out to investigate the character of the element connecting the [Ge$_8$] tubs in **2a**. Based on the results of the single crystal structure data of anion **2a**, the atom Ge5 was substituted by Ni, and the fourfold negative charge was kept. The structure refinement revealed a fused structure not congruent to the initial crystal structure data corroborating the interconnecting atom to be Ge (rather than Ni).

a)

b)

148.3°

101.5°

Ni   Ge

Ni   Ge

[Ni$_3$@Ge$_{16}$]$^{4-}$
(initial structure;
derived from crystal data)

[Ni$_3$@Ge$_{16}$]$^{4-}$
(DFT-optimized structure)
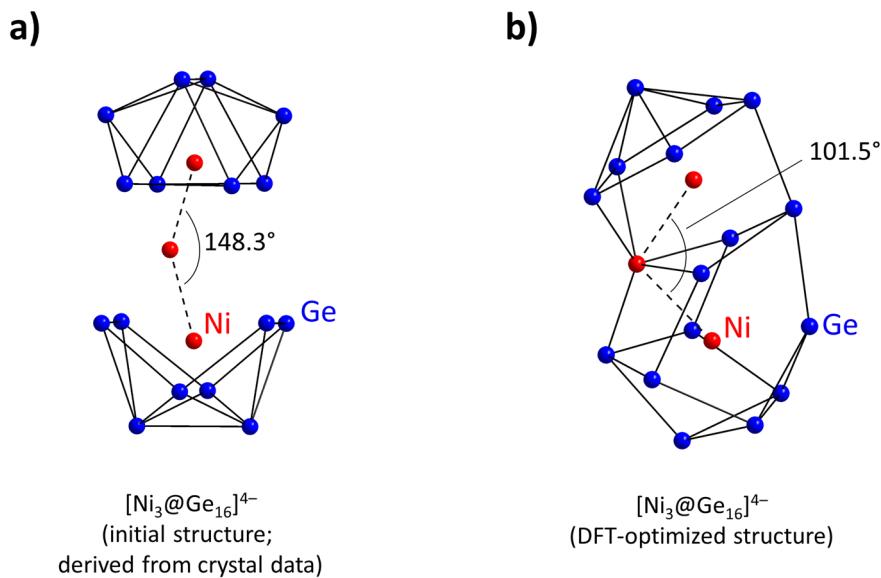
Figure S8. DFT-optimization for the theoretical anion [Ni$_3$@Ge$_{16}$]$^{4-}$. a) Initial structure with substitution of the cage-connecting atom Ge5 by Ni (derived from the single crystal structure data of anion **2a**); b) optimized structure of the theoretical anion [Ni$_3$@Ge$_{16}$]$^{4-}$.

Atomic coordinates and vibrational data

[Co₂@Ge₁₇]⁶⁻

atomic coordinates

Ge	1.3560329	-0.0065502	4.1144867
Ge	-0.0033006	2.1565276	3.2407876
Ge	-1.3560329	0.0065502	4.1144867
Ge	0.0033006	-2.1565276	3.2407876
Ge	1.9151593	-1.3239414	1.5770737
Ge	1.9311641	1.2776155	1.5819224
Ge	-1.9151593	1.3239414	1.5770737
Ge	-1.9311641	-1.2776155	1.5819224
Ge	-0.0000000	0.0000000	0.0000000
Ge	-1.2776155	1.9311641	-1.5819224
Ge	1.3239414	1.9151593	-1.5770737
Ge	1.2776155	-1.9311641	-1.5819224
Ge	-1.3239414	-1.9151593	-1.5770737
Ge	-2.1565276	-0.0033006	-3.2407876
Ge	0.0065502	1.3560329	-4.1144867
Ge	-0.0065502	-1.3560329	-4.1144867
Ge	2.1565276	0.0033006	-3.2407876
Co	0.0000000	0.0000000	2.1571425
Co	0.0000000	-0.0000000	-2.1571425

Vibrational spectrum

mode	symmetry	wave number cm⁻¹	IR intensity kJ/mol	selection rules IR	RAMAN
1		-0.00	0.00000	-	-
2		-0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	e	15.60	0.09165	YES	YES
8	e	15.60	0.09165	YES	YES
9	b	39.38	0.07528	YES	YES
10	e	46.44	0.10409	YES	YES
11	e	46.44	0.10409	YES	YES
12	a	69.87	0.00000	NO	YES
13	e	74.44	0.52083	YES	YES
14	e	74.44	0.52083	YES	YES

15	a	79.90	0.00000	NO	YES
16	b	89.72	0.04484	YES	YES
17	b	92.77	0.55718	YES	YES
18	e	94.13	0.03654	YES	YES
19	e	94.13	0.03654	YES	YES
20	a	103.01	0.00000	NO	YES
21	a	106.89	0.00000	NO	YES
22	e	108.44	0.62780	YES	YES
23	e	108.44	0.62780	YES	YES
24	b	116.51	0.20393	YES	YES
25	a	117.16	0.00000	NO	YES
26	b	120.38	2.89831	YES	YES
27	a	130.90	0.00000	NO	YES
28	b	132.78	0.60244	YES	YES
29	e	134.53	0.00145	YES	YES
30	e	134.53	0.00145	YES	YES
31	a	140.08	0.00000	NO	YES
32	b	140.53	0.19622	YES	YES
33	e	146.45	1.52459	YES	YES
34	e	146.45	1.52459	YES	YES
35	e	156.64	11.52067	YES	YES
36	e	156.64	11.52067	YES	YES
37	b	169.46	38.75330	YES	YES
38	e	172.09	14.52318	YES	YES
39	e	172.09	14.52318	YES	YES
40	b	196.97	0.16824	YES	YES
41	a	197.63	0.00000	NO	YES
42	e	200.39	2.23392	YES	YES
43	e	200.39	2.23392	YES	YES
44	a	201.79	0.00000	NO	YES
45	b	208.70	2.26865	YES	YES
46	e	213.54	1.84934	YES	YES
47	e	213.54	1.84934	YES	YES
48	a	215.36	0.00000	NO	YES
49	b	227.57	1.99460	YES	YES
50	a	230.09	0.00000	NO	YES
51	b	270.72	2.54305	YES	YES
52	e	314.98	18.18693	YES	YES
53	e	314.98	18.18693	YES	YES
54	e	361.12	47.18061	YES	YES
55	e	361.12	47.18061	YES	YES

| 56 | a | 385.67 | 0.00000 | NO | YES |
| 57 | b | 469.37 | 210.07783 | YES | YES |

K₄[Co₂@Ge₁₇]²⁻

$K_4[Co_2@Ge_{17}]^{2-}$

atomic coordinates

Ge	-4.1476467	1.1478481	-1.1047862
Ge	-3.7933833	-1.3499229	-0.3649102
Ge	-3.3706738	-0.7446066	-2.9360878
Ge	-2.3011043	1.7170288	-2.8905459
Ge	-1.5589924	2.3185322	-0.3637549
Ge	-2.4855640	0.4455914	1.1855808
Ge	-1.5362855	-2.2340971	-1.4746022
Ge	-0.6224152	-0.3491917	-3.0323931
Ge	-0.0047280	-0.1101668	-0.1938808
Ge	1.3016870	-2.2939703	1.1859579
Ge	0.2367783	-0.4346780	2.6843332
Ge	1.5038194	2.3070523	0.3570030
Ge	2.6301866	0.5446762	-1.2077902
Ge	3.6890702	-1.4367933	0.2901374
Ge	3.0992784	-0.9319332	2.8163964
Ge	4.0327310	1.0369305	1.1481984
Ge	2.0452610	1.5252809	2.8538726
Co	-1.9760046	0.0887625	-1.1120958
Co	1.8402390	0.0141906	0.9680420
K	-1.9491870	-3.2011548	1.9705887
K	1.0426230	2.7972752	-3.2719113
K	1.8398530	-2.7809648	-2.4087313
K	-1.1038570	3.0171852	3.1623387

Vibrational spectrum

mode	symmetry	wave number	IR intensity	selection rules	
		cm⁻¹	kJ/mol	IR	RAMAN
1		-0.00	0.00000	-	-
2		-0.00	0.00000	-	-
3		-0.00	0.00000	-	-
4		-0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	21.00	0.48817	YES	YES
8	a	27.20	0.42934	YES	YES
9	a	33.89	3.39896	YES	YES

10	a	36.18	0.52749	YES	YES
11	a	38.27	11.77906	YES	YES
12	a	44.94	10.66707	YES	YES
13	a	47.18	2.76524	YES	YES
14	a	51.44	0.23684	YES	YES
15	a	53.29	1.42739	YES	YES
16	a	54.16	0.12685	YES	YES
17	a	65.50	1.69950	YES	YES
18	a	67.94	6.39345	YES	YES
19	a	72.03	5.16110	YES	YES
20	a	72.84	10.82004	YES	YES
21	a	74.51	7.77268	YES	YES
22	a	75.33	7.09274	YES	YES
23	a	79.74	0.86834	YES	YES
24	a	81.17	11.84953	YES	YES
25	a	86.26	25.55502	YES	YES
26	a	87.40	15.42050	YES	YES
27	a	89.79	5.92656	YES	YES
28	a	90.46	26.98226	YES	YES
29	a	95.13	3.06232	YES	YES
30	a	97.80	21.21377	YES	YES
31	a	99.74	17.01889	YES	YES
32	a	101.29	1.20026	YES	YES
33	a	105.50	2.25921	YES	YES
34	a	108.51	2.68477	YES	YES
35	a	112.47	1.86096	YES	YES
36	a	116.77	0.08316	YES	YES
37	a	118.13	0.42756	YES	YES
38	a	121.24	1.37018	YES	YES
39	a	135.75	0.13492	YES	YES
40	a	139.97	0.06879	YES	YES
41	a	143.89	1.82066	YES	YES
42	a	146.70	2.77360	YES	YES
43	a	147.00	3.68836	YES	YES
44	a	150.73	4.87695	YES	YES
45	a	152.13	1.65690	YES	YES
46	a	154.96	4.10554	YES	YES
47	a	155.86	8.30558	YES	YES
48	a	157.74	7.38886	YES	YES
49	a	166.07	20.57558	YES	YES
50	a	173.51	11.11562	YES	YES

51	a	176.58	12.21596	YES	YES
52	a	192.63	0.59006	YES	YES
53	a	199.41	0.64662	YES	YES
54	a	200.61	2.23459	YES	YES
55	a	200.89	2.41250	YES	YES
56	a	202.73	3.42174	YES	YES
57	a	202.92	4.72449	YES	YES
58	a	205.49	0.64645	YES	YES
59	a	205.73	0.69155	YES	YES
60	a	212.36	0.06783	YES	YES
61	a	225.70	1.78546	YES	YES
62	a	231.98	0.12192	YES	YES
63	a	257.33	2.05690	YES	YES
64	a	306.44	14.69350	YES	YES
65	a	307.60	16.05865	YES	YES
66	a	357.09	30.51728	YES	YES
67	a	360.51	44.07716	YES	YES
68	a	364.50	14.13907	YES	YES
69	a	439.63	206.04614	YES	YES

[Ni$_2$@Ge$_{17}$]$^{4-}$

atomic coordinates

Ge	-0.0904626	-4.1806707	-1.2621903
Ge	1.3164729	-1.9778556	-2.0699121
Ge	2.0740268	-3.4016310	0.1189707
Ge	-2.2431026	-3.1242658	0.0219819
Ge	-0.1132455	-4.0208440	1.4541951
Ni	-0.0140932	-2.1074819	-0.0234505
Ge	0.5300271	-0.0048490	-0.4000329
Ge	-1.3106530	-1.6574565	-1.9998425
Ge	1.2160596	-1.5190146	1.9508433
Ge	-1.3511541	-1.3833792	1.8200824
Ge	1.8396178	1.7179305	1.5537735
Ge	2.2296747	1.9970337	-1.0588110
Ni	0.0309564	2.1033835	0.0080404
Ge	-1.7555836	1.4723244	-1.4566859
Ge	-1.9635036	1.3717833	1.0997029
Ge	1.2370543	4.1888995	0.2276000
Ge	-0.3135678	3.1451307	2.2033691
Ge	0.1401941	3.3726097	-2.0938694
Ge	-1.4587175	4.0083528	-0.093764

Vibrational spectrum

mode	symmetry	wave number	IR intensity	selecti on rules	
		cm^{-1}	kJ/mol	IR	RAMAN
1		-0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	19.99	0.44780	YES	YES
8	a	27.30	0.01066	YES	YES
9	a	35.75	0.07010	YES	YES
10	a	39.89	0.11450	YES	YES
11	a	47.34	0.02792	YES	YES
12	a	63.65	0.34392	YES	YES
13	a	65.57	0.01710	YES	YES
14	a	75.35	0.46010	YES	YES
15	a	81.34	0.15045	YES	YES
16	a	87.39	0.03589	YES	YES
17	a	91.02	0.53639	YES	YES
18	a	92.53	0.42975	YES	YES
19	a	98.96	1.10198	YES	YES
20	a	99.47	1.36175	YES	YES
21	a	102.84	0.28583	YES	YES
22	a	103.35	0.60777	YES	YES
23	a	109.13	1.94384	YES	YES
24	a	112.94	0.07222	YES	YES
25	a	122.76	3.14962	YES	YES
26	a	129.37	0.02850	YES	YES
27	a	130.73	0.89868	YES	YES
28	a	132.42	0.01696	YES	YES
29	a	138.98	0.47940	YES	YES
30	a	141.25	3.54189	YES	YES
31	a	141.92	1.42124	YES	YES
32	a	142.52	0.15646	YES	YES
33	a	143.86	0.16772	YES	YES
34	a	146.19	0.36600	YES	YES
35	a	148.16	0.56555	YES	YES
36	a	152.52	3.70365	YES	YES
37	a	153.35	3.79684	YES	YES

38	a	167.58	6.42386	YES	YES
39	a	169.25	5.89241	YES	YES
40	a	192.79	0.77813	YES	YES
41	a	193.01	0.61960	YES	YES
42	a	196.53	0.19297	YES	YES
43	a	198.99	2.97817	YES	YES
44	a	200.80	0.55939	YES	YES
45	a	202.78	2.25243	YES	YES
46	a	204.32	0.40238	YES	YES
47	a	205.81	0.26254	YES	YES
48	a	211.82	0.01377	YES	YES
49	a	221.79	2.80620	YES	YES
50	a	227.18	0.09801	YES	YES
51	a	251.85	0.00653	YES	YES
52	a	286.04	7.41579	YES	YES
53	a	287.14	11.01077	YES	YES
54	a	330.32	21.64704	YES	YES
55	a	330.91	28.75105	YES	YES
56	a	337.96	0.68157	YES	YES
57	a	405.96	82.97496	YES	YES

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