

[Co₂@(Ge₁₇Ni)]⁴⁻: The First Edge-Sharing Double-Cage Endohedral Germanide

Hong-Lei Xu, Lei Qiao, Zhong-Ming Sun*

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1. Experimental Procedures

All manipulations and reactions were performed under a nitrogen atmosphere using standard Schlenk or glovebox techniques. En (Aldrich, 99%) and Tol (Aldrich, 99.8%) were freshly distilled by sodium/benzophenone under N₂ atmosphere, and stored in N₂ prior to use. 2,2,2-crypt (4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo (8.8.8) hexacosane, Sigma-Aldrich, 98%) and Ni(COD)₂ (Alfa Aesar, >96%) were used as received after carefully drying them under vacuum. K₅Co_{1.2}Ge₉ was prepared according to the reported literature¹.

Synthesis of [K(2,2,2-crypt)]₄[Co₂@(Ge₁₇Ni)] (1):

In a 10 mL vial, K₅Co_{1.2}Ge₉ (88.5 mg, 0.1 mmol) and 2.2.2-crypt (95.2 mg, 0.25 mmol) were dissolved in en (2 mL). The brown-red solution was stirred vigorously for 3 h. Ni(COD)₂ (13.8 mg, 0.05 mmol) was added and stirring for 2 h again. The resulting dark-red solution was filtered through glass wool and transferred to a test tube, and then carefully layered with toluene (3 mL). After 2 weeks, black plate-like crystals of **1** were obtained at the yield of approximately 15% (23 mg) based on the used Ni(COD)₂.

X-ray Diffraction:

Suitable single crystals were selected for X-ray diffraction analyses. Crystallographic data were collected on Rigaku XtalAB Pro MM007 DW diffractometer with graphite monochromated Cu K α radiation ($\lambda = 1.54184$ Å). Structures were solved using direct methods and then refined using SHELXL-2014 and Olex2²⁻⁴ to convergence, in which all the non-hydrogen atoms were refined anisotropically during the final cycles. All hydrogen atoms of the organic molecule were placed by geometrical considerations and were added to the structure factor calculation. We used the PLATON SQUEEZE procedure⁵ to remove the solvent molecules which could not be modeled properly. CCDC entry 2111631 for compound **1** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/data_request/cif).

Electrospray Ionization Mass Spectrometry (ESI-MS) Investigations:

Negative ion mode ESI-MS of the DMF solutions of the single crystals of **1** were measured on an LTQ linear ion trap spectrometer by Agilent Technologies ESI-TOF-MS (6230). The spray voltage was 5.48 kV and the capillary temperature was kept at 300 °C. The capillary voltage was 30 V. The samples were made up inside a glovebox under a nitrogen atmosphere and rapidly transferred to the spectrometer in an airtight syringe by direct infusion with a Harvard syringe pump at 0.2 mL/ min.

Energy Dispersive X-ray (EDX) Spectroscopic Analysis:

EDX analysis on the title compound was performed using a scanning electron microscope (FE-SEM, JEOL JSM-7800F, Japan). Data acquisition was performed with an acceleration voltage of 15 kV and an accumulation time of 60 s.

Quantum chemical methods:

All calculations in this paper were performed at the PBE0/Def2-tzvp level of theory, using the GAUSSIAN 09 program package (Revision D.01).^{6, 7, 8} For geometry optimization, the solvation effects were considered by using the conductor-like polarizable continuum mode (dielectric constant (ethylenediamine) =12.9).^{9, 10, 11} The NBO analysis was performed to obtain Wiberg bond indices of bonds of the title cluster. The ELF analysis was performed via MultiWFN software.

Crystallographic Supplementary Information



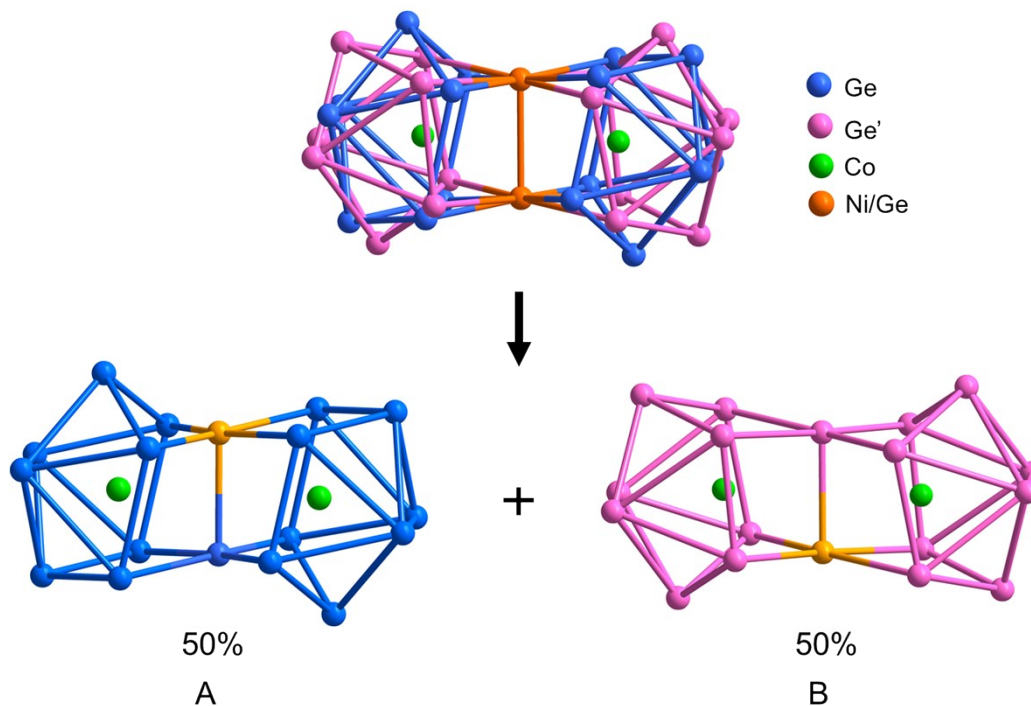
Figure S1. Crystals of [K(2,2,2-crypt)]₄[Co₂@(Ge₁₇Ni)] (**1**) dispersed silicon oil.

Table S1. X-ray measurements and structure solutions of [K(2.2.2-crypt)]₄[Co₂@(Ge₁₇Ni)].

Compound	1
Empirical formula	C ₇₂ H ₁₄₄ Co ₂ Ge ₁₇ K ₄ N ₈ NiO ₂₄
Formula weight	3072.94
Crystal system	orthorhombic
Space group	<i>Pbca</i>
<i>a</i> /Å	16.6463(3)
<i>b</i> /Å	25.7355(5)
<i>c</i> /Å	28.7503(6)
α /°	90
β /°	90
γ /°	90
<i>V</i> /Å ³	12316.7(4)
<i>Z</i>	4
ρ_{calc} /g·cm ⁻³	1.657
$\mu(\text{Cu}_{\text{K}\alpha})$ /mm ⁻¹	8.432
<i>F</i> (000)	6104.0
2 θ range /°	7.526 to 133.998
Reflections collected	68568
Data / restraints / parameters	10979/0/649
<i>R</i> ₁ / <i>wR</i> ₂ (<i>I</i> >2 σ (<i>I</i>)) ^a	0.0771, 0.2221
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.1038, 0.2433
<i>Goof</i> (all data) ^b	1.088
Data completeness	1.000
Max. peak/hole /e·Å ⁻³	2.21/-1.16

$$^a R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}; wR_2 = \left\{ \frac{\sum w[(F_o)^2 - (F_c)^2]^2}{\sum w[(F_o)^2]^2} \right\}^{1/2}$$

$$^b \text{Goof} = \left\{ \frac{\sum w[(F_o)^2 - (F_c)^2]^2}{(n-p)} \right\}^{1/2}$$



Structural refinement reveals that the two embedded Co atoms are well-ordered, while 16 Ge atoms in both cages are disordered at two sets of positions (marked as blue and pink). Additionally, each one of the two atomic sites from shared edge are co-occupied by Ni and Ge with 50% possibility, respectively, and the corresponding sites are shown as the orange (Ge/Ni) for clarity. The disordered cluster sites are divided into two groups (blue for **A** and pink for **B**) with 50% occupancy each other. The two components (**A** and **B**) were successfully modeled and were shown to be almost identical from a geometric perspective. Each component can be considered as a double-cage cluster containing two ten-vertex endohedral $[\text{Co}@(\text{Ge}_9\text{Ni})]$ subunits featuring a centaur polyhedron which are combined by sharing a Ge-Ni edge in an up-down mode. Nothing that the up-down only represents the relative orientation of two centaur polyhedral subunits $[\text{Co}@(\text{Ge}_9\text{Ni})]$ in the structure of cluster anion.

Figure S2. Disorder model shown as both compositions with 50% occupancy, respectively.

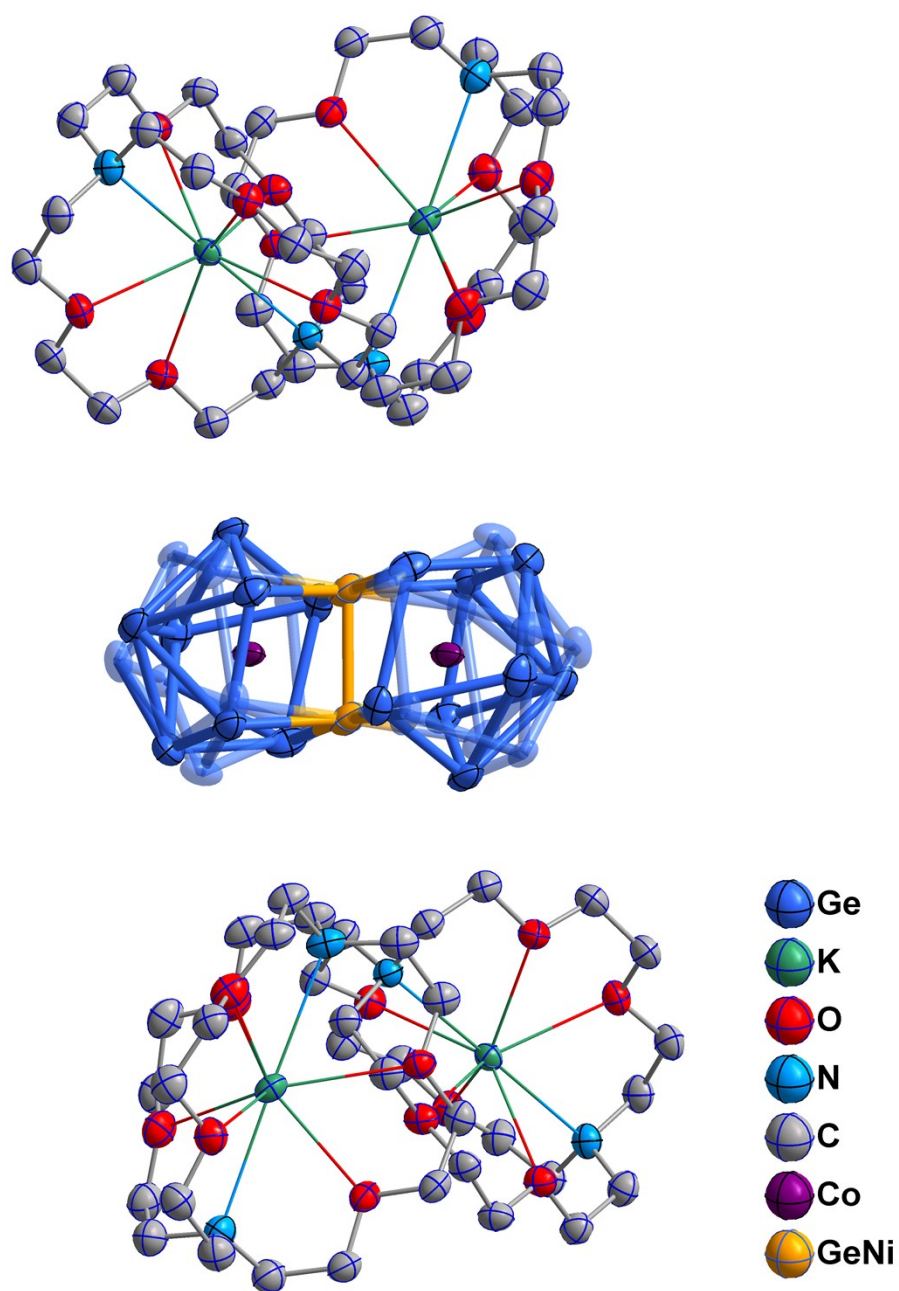


Figure S3. Asymmetric unit of **1** with the cluster fragment. Thermal ellipsoids are drawn at 50% probability. The minor components are omitted for clarity. The disordered components are shown at 50% transparency. The H atoms are omitted for clarity.

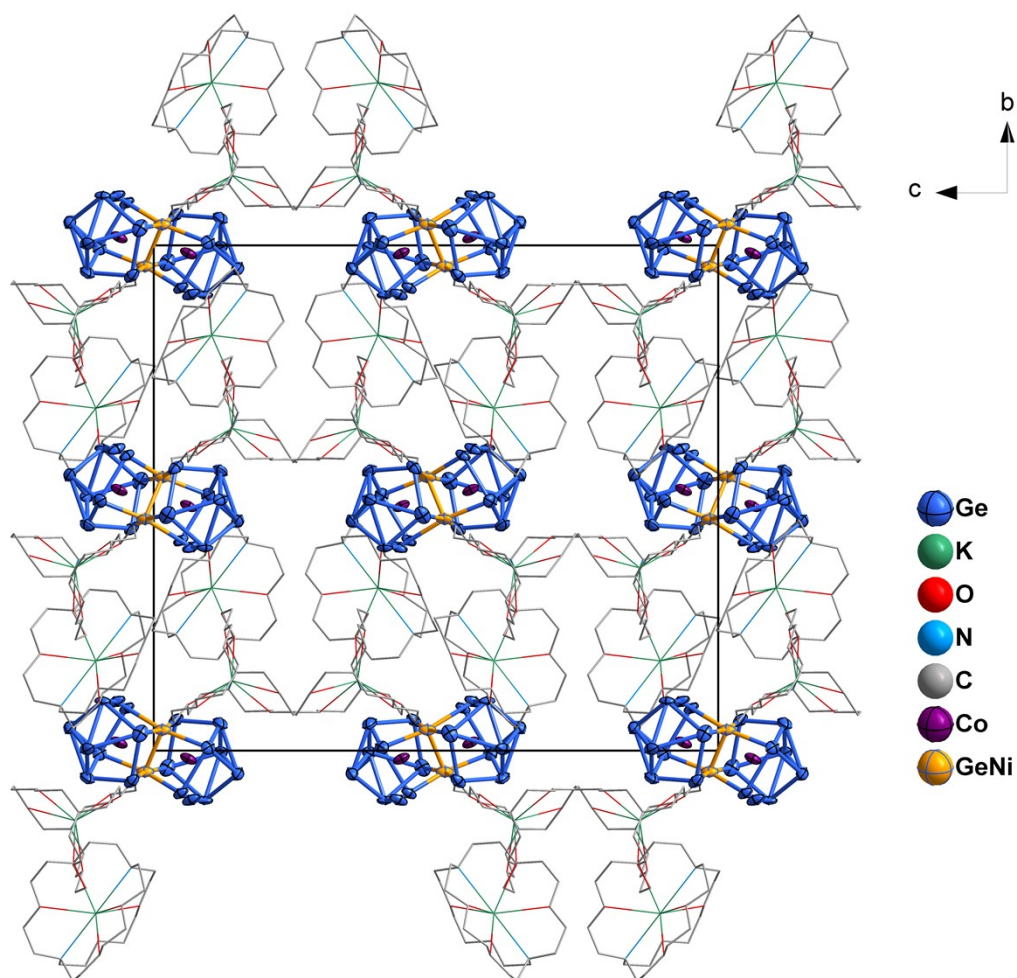


Figure S4. Unit cell of compound **1**. Minor components and disordered sites in the structure are omitted for clarity.

2. ESI-MS Studies

The ESI-MS of the DMF solution of the crystals of **1** was analyzed and shown in the **Figures S5**. Measured and simulated isotope distributions for all species were shown in the **Figures S6-9**.

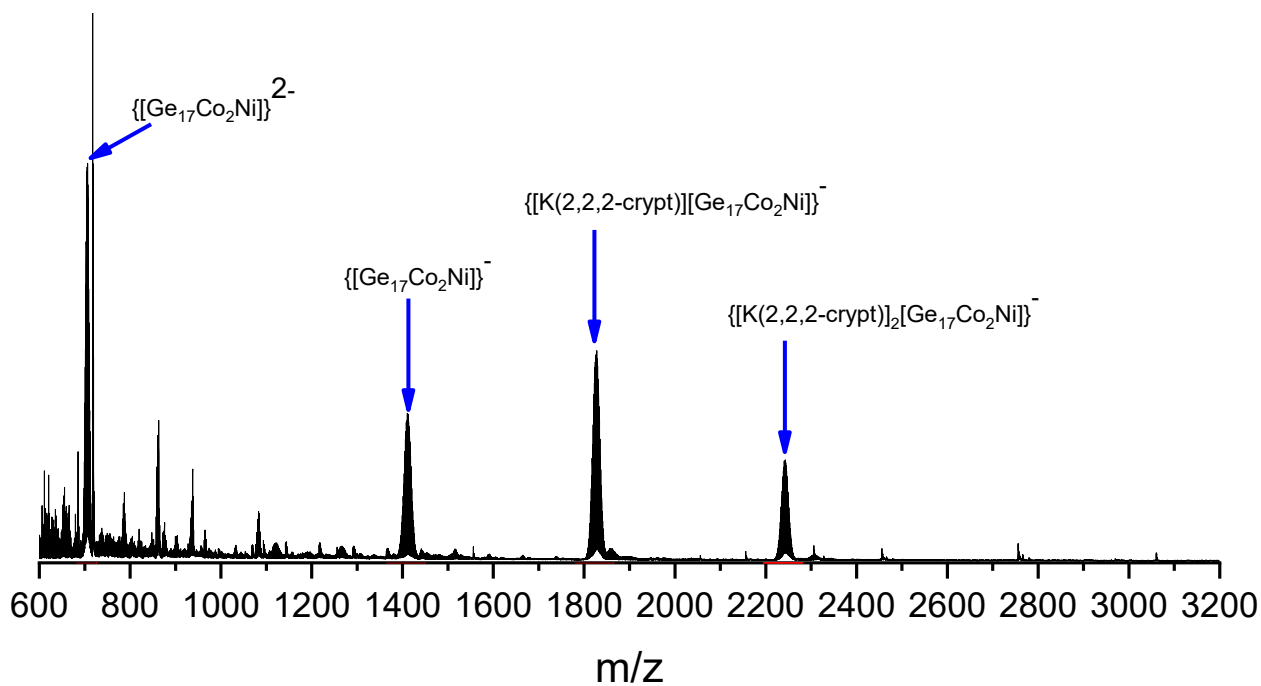


Figure S5. Overview ESI mass spectrum in negative ion mode of a freshly dissolved crystalline sample of **1** in DMF.

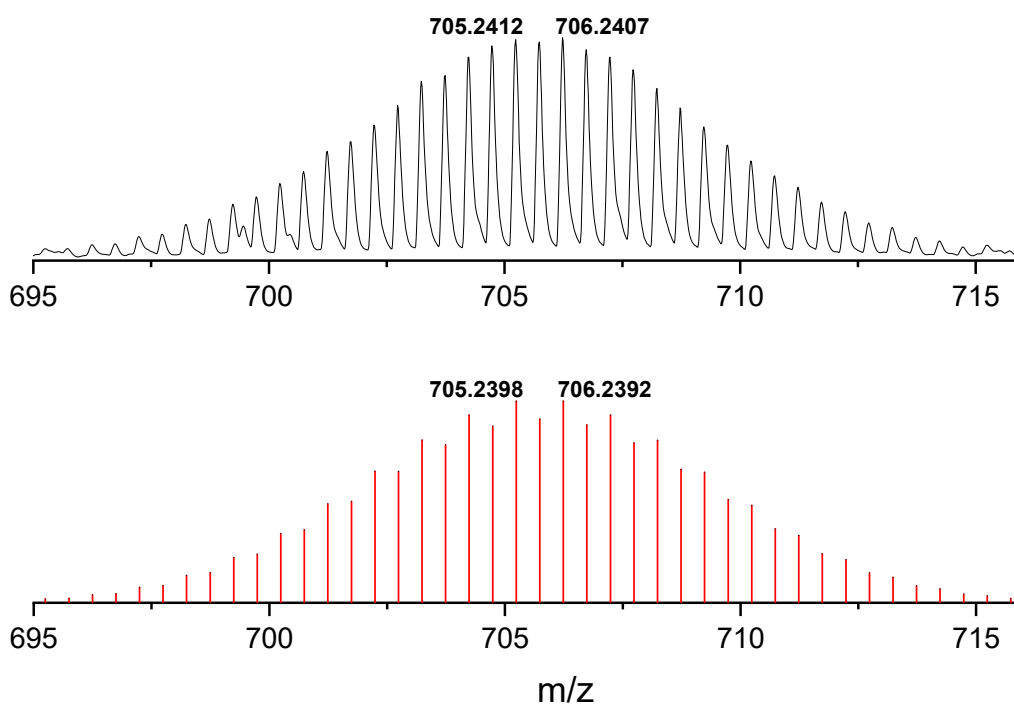


Figure S6. Measured (black) and simulated (red) spectrum of the fragment $\{[Ge_{17}Co_2Ni]\}^{2-}$.

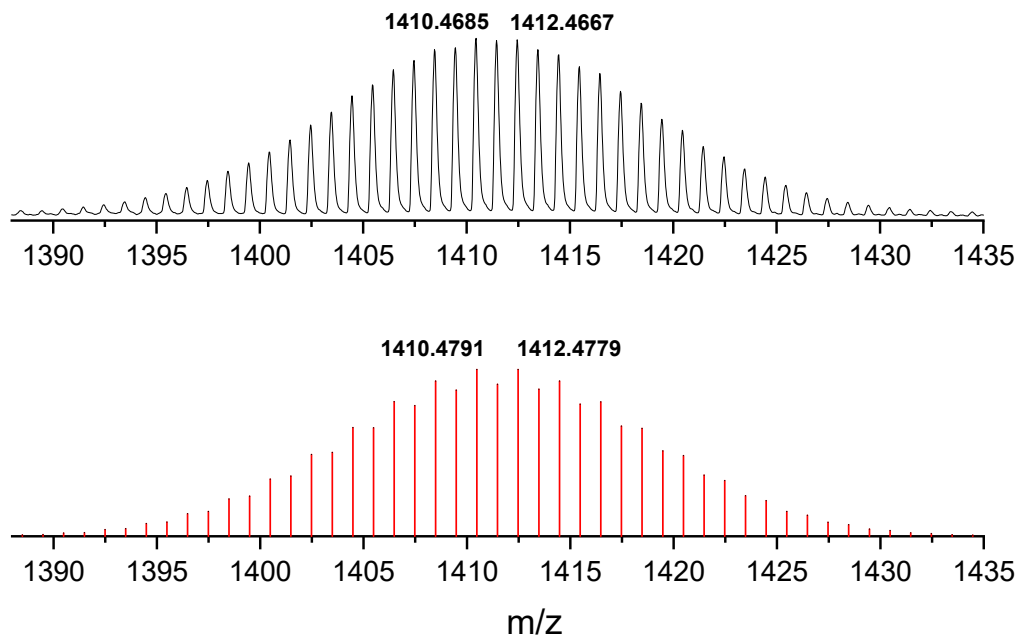


Figure S7. Measured (black) and simulated (red) spectrum of the fragment $\{[Ge_{17}Co_2Ni]^{-}\}$.

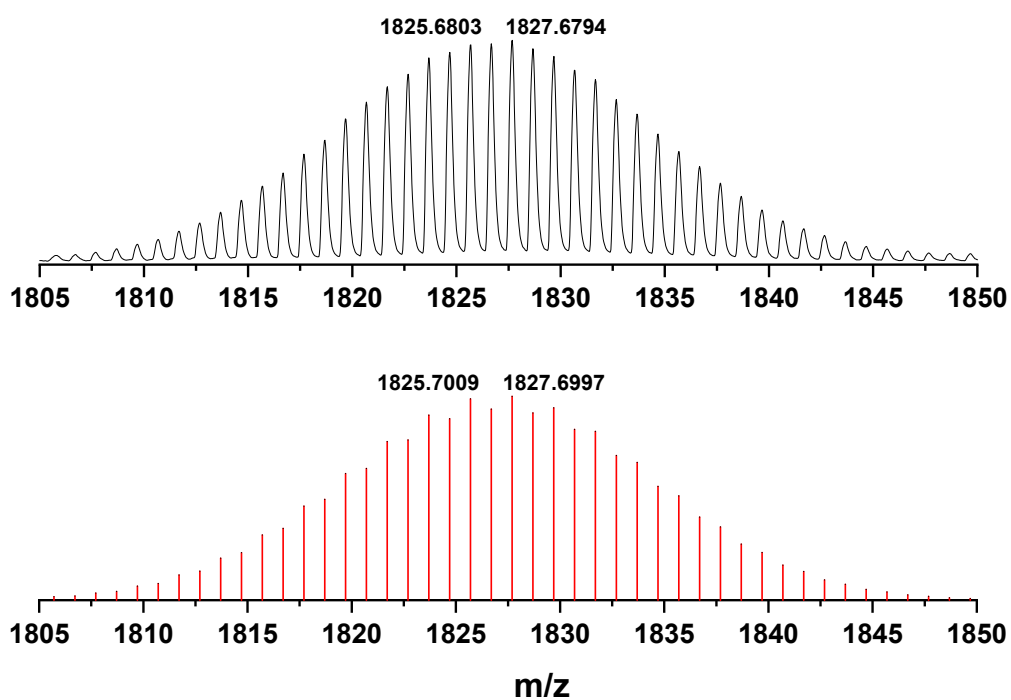


Figure S8. Measured (black) and simulated (red) spectrum of the fragment $\{[K(2,2,2\text{-crypt})][Ge_{17}Co_2Ni]^{-}\}$.

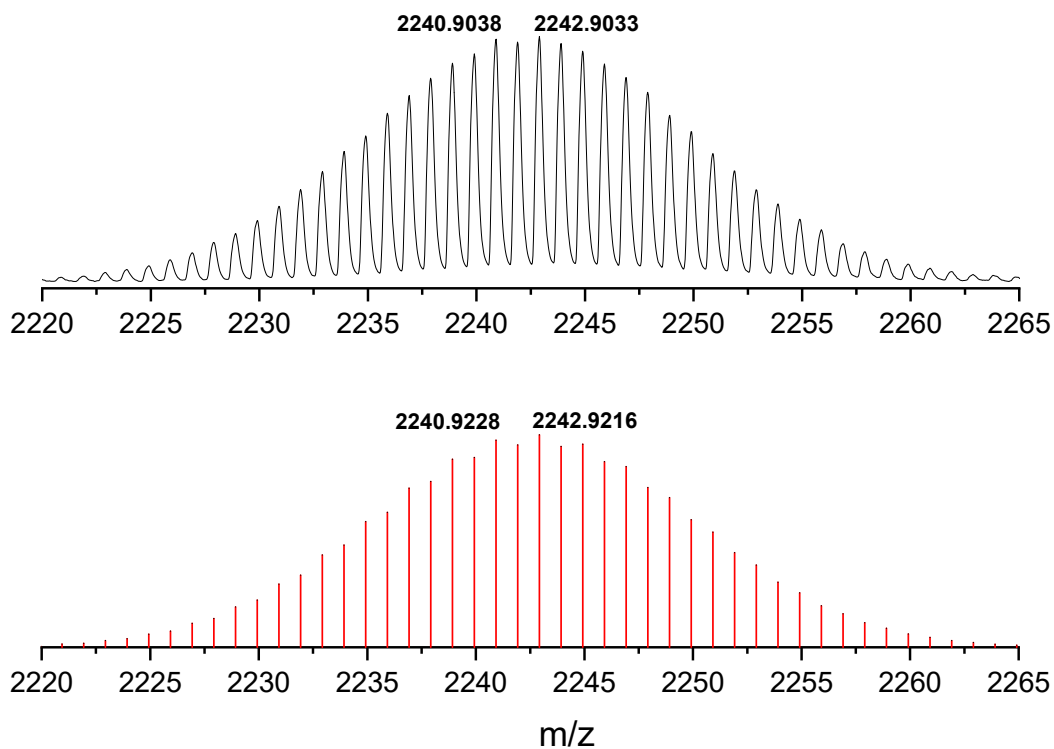


Figure S9. Measured (black) and simulated (red) spectrum of the fragment $\{[K(2,2,2\text{-crypt})]_2[Ge_{17}Co_2Ni]\}^-$.

3. Energy Dispersive X-ray (EDX) Spectroscopic Analysis

The result of EDX analysis on compound **1** was presented in **Figures S10**. The atom% values of K:Co:Ge:Ni are shown as 12.4%:5.9%:78.0%:3.6% compared with the theoretical values of $K_4Co_2Ge_{17}Ni$ (10.0%:7.5%:78.8%:3.7%). A deviation of the amount of K/Co is observed in the EDX characterization, which may be caused by the irregular surfaces of the crystals after exposing in air.

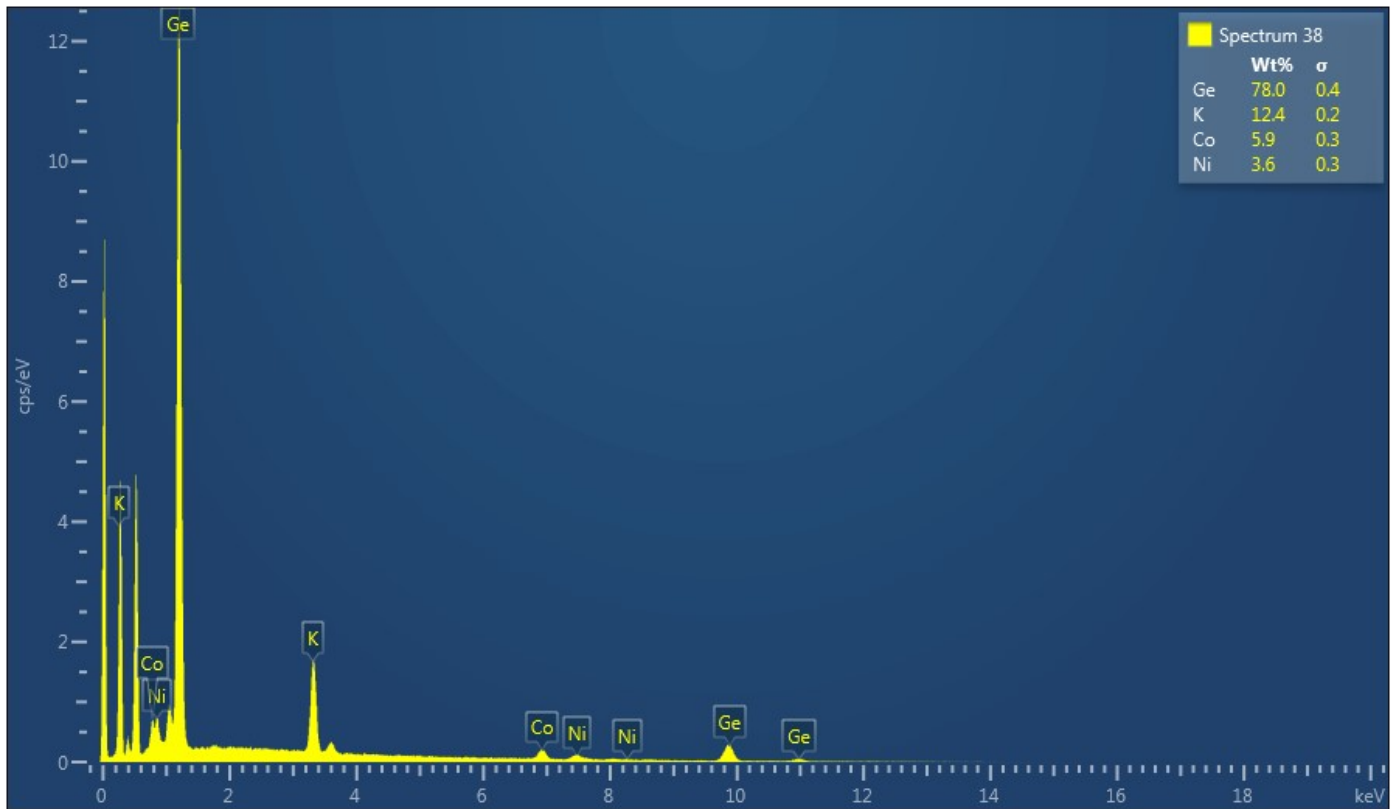


Figure S10. EDX analysis of 1.

4. Computational Details

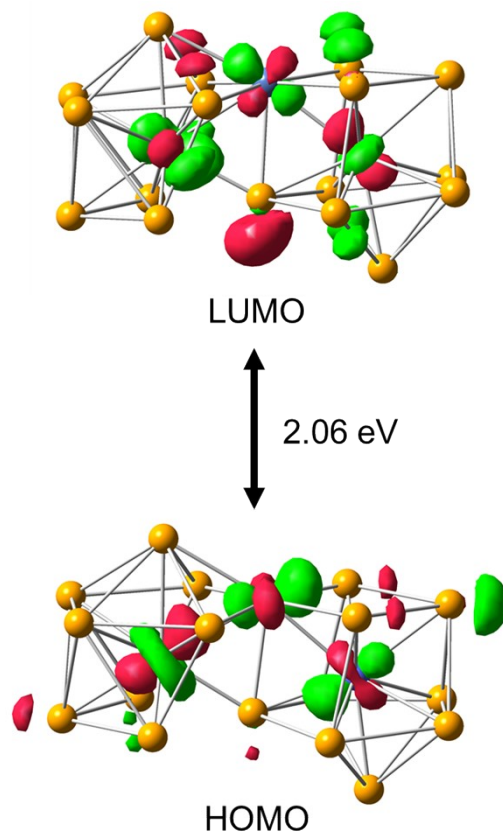


Figure S11. The calculated HOMO-LUMO gap in **1a** (Isovalue for density surfaces: 0.04).

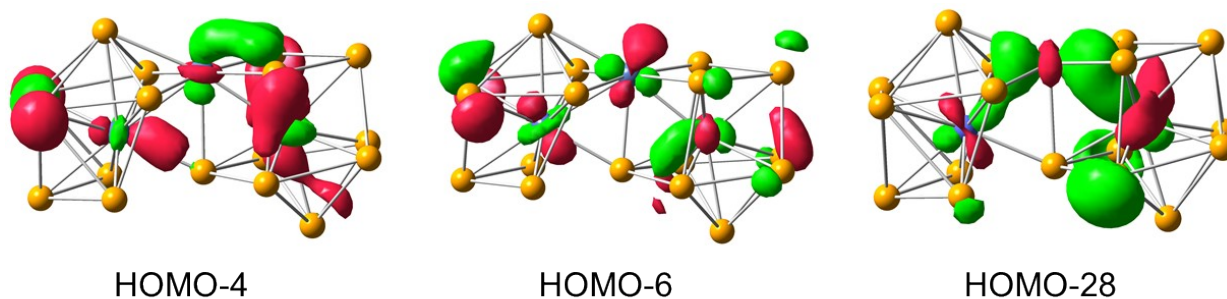


Figure S12. Selected frontier molecular orbitals of **1a** (Isovalue for density surfaces: 0.04).

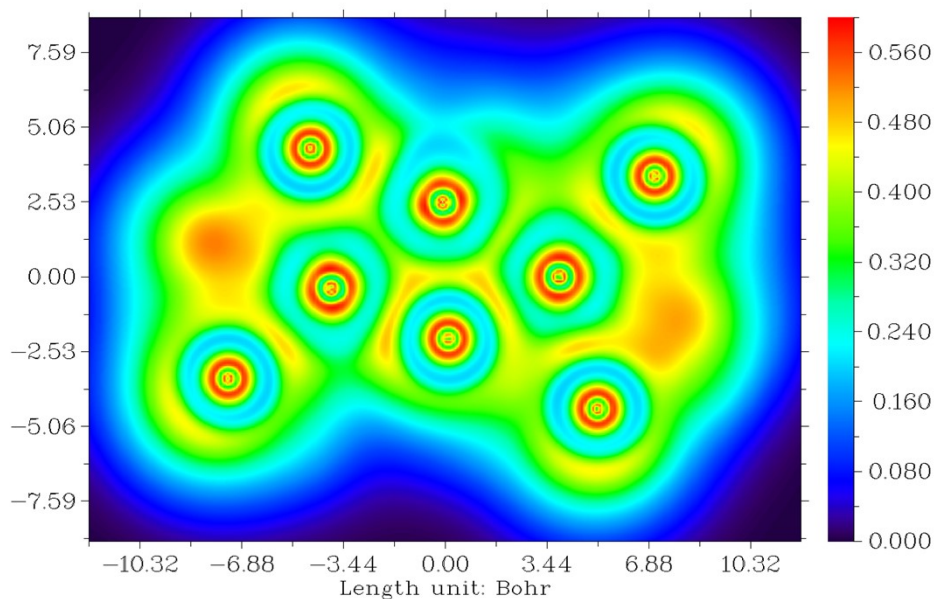


Figure S13. ELF plots of **1a**. plot is built in the plane of rhombus-like $[\text{Co}_2\text{GeNi}]$.

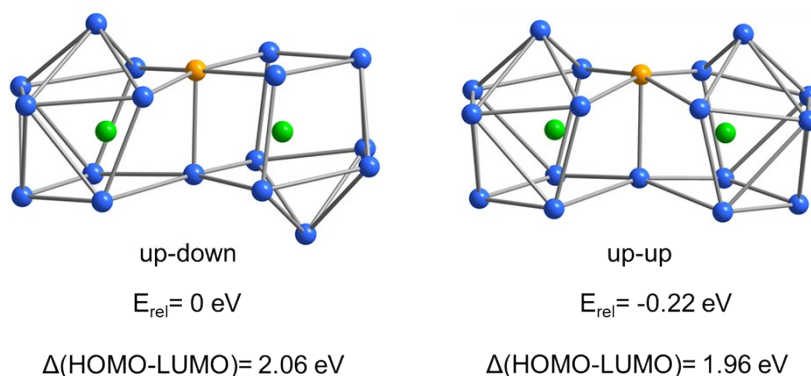


Figure S14. Optimized structures of the up-down and up-up isomers of the title cluster anion. The isomer with an up-up mode was also considered according to the analysis of DFT calculations. We are able to locate distinct minima with up-down and up-up isomers, both shown in Figure S14, with Ni-Ge, Co-Ni and Co-Ge bond lengths are in good agreement with those in the crystal structures (within 0.1 Å). The energy gap between the both isomers is very narrow (0.22 eV, 5.07 kcal/mol), demonstrating that the gas-phase potential energy surface is flat. The rather low barrier of 5.07 kcal/mol indicates that the cluster anion should be highly fluxional, at least in the gas phase. The very similar energies and bond lengths for both isomers suggest that the transition between them is achievable in solution. Additionally, both isomers show similar HOMO-LUMO gaps with a somewhat larger value (2.06 eV) for up-down mode than one (1.96 eV) for up-up mode. However, according to the point of crystallographic structure, the disorder was successfully modeled and divided into two components with an up-down mode shown in Figure S2. Overall, the isomer with an up-up mode is possible to crystallize under the suitable condition, but in the present crystal structure, the one with an up-down mode is able to be modelled clearly.

Table S2. Optimized atomic coordinates of **1a**.

Center Number	Atomic type	Coordinates (Angstroms)		
		X	Y	Z
1	Co	2.052427	0.002488	0.012420
2	Ni	-0.032977	-0.006931	1.339014
3	Ge	0.062015	0.011587	-1.096894
4	Co	-2.030386	0.000915	-0.194688
5	Ge	1.728770	-1.662186	1.590189
6	Ge	1.564993	-2.186348	-1.035186
7	Ge	4.048225	1.317510	-0.495310
8	Ge	3.758860	0.013206	1.816253
9	Ge	2.734532	-0.013605	-2.349649
10	Ge	1.583060	2.189192	-1.048130
11	Ge	4.039701	-1.333074	-0.478084
12	Ge	1.713601	1.671474	1.580281
13	Ge	-1.333670	2.046287	0.995998
14	Ge	-2.403171	-0.007879	2.306275
15	Ge	-1.335442	-2.054037	0.981859
16	Ge	-2.148206	1.942184	-1.514854
17	Ge	-2.144339	-1.931419	-1.527803
18	Ge	-3.990173	-1.317418	0.528799
19	Ge	-3.990773	1.313131	0.537972
20	Ge	-3.877726	0.004589	-1.809563

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