Supporting Information

[Ge₅Ni₂(CO)₃]²⁻ : The First Functionalized Cluster of *closo*-

$[Ge_5]^{2-}$

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1 Experimental Details

1.1 General Procedures

All manipulations and reactions were performed in a nitrogen atmosphere using standard Schlenk or glovebox techniques. Ethylenediamine (en) (Aldrich, 99%) and Acetonitrile(MeCN) were freshly distilled by CaH_2 prior to use. Toluene (tol) (Aldrich, 99.8%) was distilled from sodium/benzophenone under dinitrogen and stored under dinitrogen. [2.2.2]-crypt (4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo [8.8.8]hexacosane, purchased from Sigma-Aldirich, 98%) were dried in vacuum for one day prior to use. Ni(CO)₂(PPh₃)₂ (Alfa-Aesar, 98%) was used as received as received after carefully drying them under vacuum. "KGe_{1.67}" was synthesized according to method described in the literature.¹

1.2 Synthesis of [K([2.2.2]crypt)]₂[Ge₅Ni₂(CO)₃)]•en (1)

In a 10 mL vial, the alloy with the nominal composition "KGe_{1.67}" (80 mg) and 2.2.2-crypt (50 mg, 0.16 mmol) were weighed out into a test tube and dissolved in 2 mL of ethylenediamine, producing a red solution. This solution was stirred for 30 min, after

which Ni(PPh₃)₂(CO)₂ (128 mg, 0.2 mmol) was added directly and allowed to stir for 20 min. The dark brown solution was then slightly heated for 6 h at 35 °C. This solution was centrifuged, filtered through glass wool and transferred to a test tube, then carefully layered by toluene to allow for crystallization. It yielded dark block crystals of $[K(2,2,2-crypt)]_2[Ge_5Ni_2(CO)_3]$ •en after 5 days (yield ca. ~10%, based on employed KGe_{1.67}).

2 X-ray Diffraction Measurements, Structure Solution and Refinement of

$[K([2.2.2]crypt)]_{2}[Ge_{5}Ni_{2}(CO)_{3})]$ •en

2.1 X-ray diffraction measurements and structure solution of [K([2.2.2]crypt)]₂[Ge5Ni₂(CO)₃)]•en

Single crystal X-ray diffraction data of $[K([2.2.2]crypt)]_2[Ge_5Ni_2(CO)_3)]$ •en (Table Sı) was collected on a Rigaku RAXIS-RAPID equipped with a narrow-focus, 5.4 kW sealed tube X-ray source (graphite-monochromated Mo K α radiation, λ =0.71073 Å) at 150 K. Data processing was accomplished with the PROCESS-AUTO processing program. The SHELXTL program package ²⁻³ and Olex₂⁴ was implemented for data processing, structure solution, and refinement. The structure was determined by direct methods (XS) with the successful location of the heavy atoms comprising the cluster. After the initial refinement difference Fourier cycle, additional atoms were located and input. The most significant residual electron density for $[K([2.2.2]crypt)]_2[Ge_5Ni_2(CO)_3)]$ •en was located at the cluster anion site. In contrast, the $[K(2,2,2-crypt)]^+$ cations and en molecules appear to be well-behaved. Two different orientations were found for the cluster. The final max/min ratio was 0.76:0.24. Hydrogen atoms were placed in calculated positions. The final structure was refined to convergence. CCDC 1538039 contains 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.

Table S1. X-ray measurements and structure solution of compound 1.

Compound	$C_{41}H_{80}N_6O_{15}K_2Ni_2Ge_5$
Formula weight	1455.68

Crystal system	Triclinic
Space group	P-1
a /Å	10.8950(3)
b/Å	13.520(3)
c /Å	21.603(16)
α /°	95.330(3)
β /°	95.484(3)
γ /°	110.884(3)
V	2923.5(8)
Ζ	2
$\rho_{\rm calc}/{\rm g}\cdot{\rm cm}^{-3}$	1.654
$\mu(Mo_{K\alpha}) / mm^{-1}$	3.370
2Θ range /°	3.26-52.234
Reflections collected / unique	18278/11478
Data / restraints / parameters	11478/6/693
Final <i>R</i> indices $(I > 2\sigma(I))^a$	$R_1 = 0.0536, wR_2 = 0.1067$
R indices (all data)	$R_1 = 0.1047, wR_2 = 0.1260$
GooF (all data) ^b	1.057
Data completeness	0.986
Max. peak/hole /e ⁻ ·Å ⁻³	2.72/-2.27

^{*a*} $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|; wR_2 = \{\sum w[(F_0)^2 - (F_c)^2]^2 / \sum w[(F_0)^2]^2 \}^{1/2}$

 ${}^{b}\operatorname{GooF} = \{\sum w[(F_{\rm o})^{2} - (F_{\rm c})^{2}]^{2}/(n-p)\}^{1/2}$

2.2 Structure of [K([2.2.2]crypt)]₂[Ge₅Ni₂(CO)₃)]•en



Figure S1. Unit cell of $[K([2.2.2]crypt)]_2[Ge_5Ni_2(CO)_3)]$ •en. Hydrogen atoms have been omitted for clarity.



The cluster $[Ge_5Ni_2(CO)_3)]^{2-}$ adopts two different orientations, including a major component (dimajor, pictured as dark bonds) and a minor component (dimin, pictured as yellow bonds) related by rotation about the Ge-Ge edge adjacent to the Ni₂(CO)₃ fragment. This gave rise to a model with a 74:26 ratio of major to minor cluster site occupancy.

Figure S2. The observed disorder in clusters [Ge₅Ni₂(CO)₃)]²⁻.

Table S2. Selected interatomic distances (in angstroms) of the experimental and optimized structures of *i* at the Def2-TZVP level of theory.

	Calculated	Experiment		Calculated	Experiment
Ge(1)-Ge(2)	2.64700	2.5608(12)	Ni (1)-Ge(1)	2.53820	2.5262(17)
Ge(1)-Ge(3)	2.77873	2.7675(11)	Ni(1)-Ge(3)	2.54142	2.5036(11)
Ge(1)-Ge(4)	2.58341	2.595(3)	Ni(1)-Ge(4)	2.60337	2.587(2)
Ge(1)-Ge(5)	2.58144	2.5693(14)	Ni(2)-Ge(1)	2.54161	2.5076(18)
Ge(2)-Ge(3)	2.64601	2.5743(14)	Ni(2)-Ge(3)	2.53594	2.5030(15);
Ge(2)-Ge(5)	2.56775	2.5024(11)	Ni(2)-Ge(5)	2.60495	2.5785(16)
Ge(2)-Ge(4)	2.56689	2.516(4)	Ni(2)-Ge(3)	2.53594	2.5560(8)
Ge(3)-Ge(4)	2.58341	2.576(2)	Ni(1)-Ni(2)	2.42096	2.4020(15)
Ge(3)-Ge(5)	2.58399	2.5802(15)			

3 Energy Dispersive X-ray (EDX) Spectroscopy Analysis

EDX analysis on $[K([2.2.2]crypt)]_2[Ge_5Ni_2(CO)_3)]$ en (Figure S5) was performed on the Energy Disperse Spectroscopy (EDS). The spectrum was obtained by using a scanning electron microscope (Hitachi S-4800) equipped with a Bruker AXS XFlash detector 4010. The atomic ratio of K/Ni/Ge is 2:1.88:5.5, which is in good agreement with the experimental crystallographic data.



Figure S3. EDX analysis of $[K([2.2.2]crypt)]_2[Ge_5Ni_2(CO)_3)]$ en (K, Ni, Ge).

4. Powder X-ray Diffraction Pattern of the precursor with a nominal composition "KGe_{1.67}".



Figure S4: Powder X-ray diffraction pattern (top) of the precursor with a nominal composition "KGe_{1.67}". The simulated pattern (bottom) of K₄Ge₉ was present for reference. The experimental pattern indicates that there are a few unknown phases beside the phase K_4 Ge₉.

5. Electrospray Ionization Mass Spectrometry (ESI-MS)

Positive and negative ion mode electrospray mass spectra were performed on LTQ linear Ion Trap Spectrometer. The spray voltage was 5.48 kV and the capillary temperature was keep at 300 °C. The capillary voltage was 30V. The samples were made up inside a glovebox under an inert atmosphere and rapidly transferred to the spectrometer in an air-tight syringe by direct infusion with a Harvard syringe pump at 15 *u*L/ min. The $KGe_{1.67}/Ni(PPh_3)_2(CO)_2$ /2.2.2-crypt/en reaction solution was prepared according to the synthesis described for $[K([2.2.2]crypt)]_2[Ge_5Ni_2(CO)_3)]$ •en. The crystals of $[K([2.2.2]crypt)]_2[Ge_5Ni_2(CO)_3)]$ •en were dissolved in CH₃CN.



Figure S5. The full electrospray mass spectrum (m/z: 500 – 1500) in negative ion mode of the reaction solution producing $[Ge_5Ni_2(CO)_3)]^{2-}$.



Figure S6. Negative ion-mode electrospray mass-envelope corresponding to {[Ge₉Ni₂(CO)]}-

and $\{[K(2,2,2-crypt)][Ge_9Ni_2(CO)]\}^-$. Recorded experimental data are given in red with the calculated isotopic distribution in dark.



Figure S7. Negative ion-mode electrospray mass-envelope corresponding to [Ge₅Ni₂(CO)]}⁻. Recorded experimental data are given in red with the calculated isotopic distribution in dark.



Figure S8: The full electrospray mass spectrum (m/z: $_{300}$ – $_{500}$) in negative ion mode of the reaction solution producing [Ge₅Ni₂(CO)₃)]²⁻.



Figure S9. Negative ion-mode electrospray mass-envelope corresponding to $[Ni_2(CO)_3(PPh_2)]$ ⁻, $[Ni_2(CO)_2(PPh_2)]$ ⁻, and $[Ni_2(CO)(PPh_2)]$ ⁻. Recorded experimental data are given in red with the calculated isotopic distribution in green.



Figure S10. Negative ion mode ESI-MS of freshly dissolved crystals of 1 in MeCN.



Figure S11. Section of the electrospray mass spectrum of freshly dissolved crystals of 1 in MeCN. (in negative-ion mode; calculated peaks shown in green)



Figure S12. Positive ion mode ESI-MS of freshly dissolved crystals of 1 in MeCN.



Figure S13. Section of the electrospray mass spectrum of freshly dissolved crystals of 1 in MeCN. (in positive-ion mode; calculated peaks shown in green)



Figure S14: The full electrospray mass spectrum (m/z: 350-1500) in negative ion mode of the en solution of the phase "KGe_{1.67}" in the presence of 2,2,2-crypt.



ure S15: Negative ion-mode electrospray mass-envelope corresponding to [Ge₅]⁻ and [KGe₅]⁻

. Recorded experimental data are given in red with the calculated isotopic distribution in dark.



ure S16: Negative ion-mode electrospray mass-envelope corresponding to $[Ge_9]^-$ and $[KGe_9]^-$. Recorded experimental data are given in red with the calculated isotopic distribution in dark.



Figure S17: Negative ion-mode electrospray mass-envelope corresponding to $[Ge_6]^-$, $[Ge_7]^-$ and $[Ge_8]^-$. Recorded experimental data are given in red with the calculated isotopic distribution in dark.



6. IR spectrum of the crystal [K([2.2.2]crypt)]₂[Ge₅Ni₂(CO)₃)]•en

Figures S18: IR spectrum of the crystal $[K([2.2.2]crypt)]_2[Ge_5Ni_2(CO)_3)]$ •en in Nujol mulls, which cuts out the absorption of background.

7. Computational Methods and Details

Geometry optimization and frequency calculations of $[Ge_5]^{2^-}$, $[Ge_5Ni_2(CO)_3]^{2^-}$ and neutral (u-CO)Ni_2(CO)_2 were respectively performed at the PBEo/Def2-TZVP level of theory⁵ by Gaussian o9 software package⁶. Optimized geometrical structures of $[Ge_5]^{2^-}$ and $[Ge_5Ni_2(CO)_3]^{2^-}$ were found to be similar to those found in the real crystal as shown in Table S2. And the calculated Wiberg bond indices were in line with their bond distances in $[Ge_5Ni_2(CO)_3]^{2^-}$ cluster (Table S3). Natural population analysis (NPA) ⁷ was performed to identify the charge transfer. The calculated natural charge for Ni₂ species in neutral (u-CO)Ni₂(CO)₂ was as low as 0.04 |e|, whereas, the natural charge for Ni₂ species between $[Ge_5Ni_2(CO)_3]^{2^-}$ is of -1.68 |e|. The difference of charge density for Ni₂ species between $[Ge_5Ni_2(CO)_3]^{2^-}$ and neutral (u-CO)Ni₂(CO)₃]^{2^-} and neutral (u-CO)Ni₃(CO)₃]^{2^-} and neutral (u-CO)Ni₃(CO)₃]^{2^-}

Table S3. Calculated Wiberg bond indices of $[Ge_5Ni_2(CO)_3]^2$ ⁻² and $[Ge_5]^2$ ⁻² at the PBEo with basis sets of def2-TZVP.

[Ge ₅ Ni ₂ (CO) ₃] ²⁻		[Ge ₅] ²⁻			
Ge1-Ge2	Ge1-Ge3	Ge2-Ge3	Ge1-Ge2	Ge1-Ge3	Ge2-Ge3	

0.83	0.70	0.83	0.95	0.95	0.95
Ge2-Ge5	Ge1-Ge5	Ge3-G5	Ge2-Ge5	Ge1-Ge5	Ge3-G5
1.06	0.87	0.87	1.22	1.22	1.22
Ge2-Ge4	Ge1-Ge4	Ge3-Ge4	Ge1-Ge4	Ge2-Ge4	Ge3-Ge4
1.06	0.87	0.87	1.22	1.22	1.22
Ge1-Ni1	Ge3-Ni1	Ge4-Ni1			
0.60	0.60	0.66			
Ge1-Ni2	Ge3-Ni2	Ge5-Ni2			
0.60	0.60	0.66			

Detailed AdNDP results.

Chemical bonding analyses of $[Ge_5]^{2-}$ and $[Ge_5Ni_2(CO)_3]^{2-}$ were performed via the Adaptive Natural Density Partitioning method at the PBEo/Def2-TZVP level of theory. All the AdNDP calculations were performed using the Gaussian o9 software package and analyzed by the Multiwfn 3.3.9 software package⁸. Orbital visualizations were performed using VMD 1.9.1⁹.

In total, there are 72 valence electrons (36 pairs) in the $[Ge_5Ni_2(CO)_3]^{2-}$ cluster, whereas, there are 22 valence electrons (11 pairs) in the Ge_5^{2-} cluster. AdNDP transformed all these canonical molecular orbitals into the nc–2e bonding elements presented below.

a)
$$[Ge_5Ni_2(CO)_3]^{2-1}$$

Firstly, it found the following lone pairs (1c-2e) and classical (2c-2e) bonds:

- 1) Five d-type LPs on two Ni atoms with ON=1.84-1.98 |e| (Figure S19A)
- 2) Five s-type LPs on 5 apical Ge atoms with ON=1.92-1.98 |e| (Figure S19B)
- 3) Three s-type LPs on each O atoms with ON=1.98 |e| (Figure S19C)
- 4) One 2c-2e C-O σ bonds with ON=2.00 |e| on each CO group (Figure S19D)
- 5) Two 2c-2e π bonds with ON=1.99 |e| on each CO group (Figure S19E)
- 6) One 2c-2e Ni-C σ bond with ON=1.92 |e| (Figure S19F)

Secondly, there are One 3c-2e Ni-C-Ni σ bond with ON = 1.90 |e| (Figure S19G) and four 3c-2e Ge-Ge-Ge σ bonds with ON = 1.88 |e| (Figure 3B). Finally, two 4c-2e Ge-Ge-Ge-Ni σ bonds with ON = 1.84 |e| were found (Figure 3B). These bonds are formed by the interaction of p-orbitals of Ge with d-orbitals of Ni. Essentially, they can also be viewed as two pure 3c-2e Ge-Ge-Ge σ bonds because the contribution of the Ge₃-electron density is assessed to be high to 81%.

b) [Ge₅]²⁻

There are 5 s-type LPs on 5 apical Ge atoms with ON=1.92-1.95 |e| (Figure S19H) and 6 3c-2e delocalized σ bonds on each Ge₃ face (Figure 3A).



Figure S19 A) Five d-type LPs on each Ni atom in $[Ge_5Ni_2(CO)_3]^{2-}$; B) Five s-type LPs on five apical Ge atoms in $[Ge_5Ni_2(CO)_3]^{2-}$; C) three s-type LPs on each O atom; D) three 2c-2e C-O σ bonds; E) Six 2c-2e C-O π bonds; F) Two 2c-2e Ni-C σ bonds; G) One 3c-2e Ni-Ni-C σ bond; H) Five s-type LPs on five apical Ge atoms in $[Ge_5]^{2-}$.

[Ge ₅ Ni ₂ (C	CO) ₃] ²⁻		
-2	1		
Ge	-0.425469	-0.002187	-0.002187
Ge	-0.425186	0.001720	0.001720
Ge	-1.135208	-2.059296	-2.059296
Ge	-2.677789	-0.007625	-0.007625
Ge	-1.146928	2.053878	2.053878
Ni	1.324835	-1.207391	-1.207391
Ni	1.318744	1.213531	1.213531
0	3.939418	0.008643	0.008643
0	2.465463	3.857983	3.857983
C	2.010891	2.795272	2.795272
C	2.764151	0.006283	0.006283
0	2.484975	-3.846509	-3.846509
C	2.024877	-2.784978	-2.784978
$[Ge_5]^{2-}$			
-2	1		
Ge	0.000000	0.000000	0.000000
Ge	-1.363691	-1.363691	0.000000
Ge	0.000000	0.000000	1.970874
Ge	1.363691	1.363691	0.000000
Ge	0.000000	0.000000	-1.970874
$Ni_2(CO)_3$			
0	1		
Ni	-1.203116	-0.360033	-0.002695
Ni	1.203116	-0.360041	-0.000449
0	0.000042	2.171287	-0.000919
0	4.083679	-0.031860	0.003757
C	2.965419	-0.232305	0.001986
C	-0.000033	1.014854	-0.001227
0	-4.083685	-0.031853	0.005981
C	-2.965434	-0.232303	0.002154

Table S4. Cartesian coordinates of $[Ge_5Ni_2(CO)_3]^{2-}$, $[Ge_5]^{2-}$, and $Ni_2(CO)_3$ at the PBEo/Def2-TZVP level of theory

References

- 1. Suchentrunk, C., Korber, N., New J. Chem., 2006, 30, 1737-1739.
- 2. Sheldrick, G.M., *Acta Cryst.* 2008, *A64*, 112-122.
- 3. Sheldrick, G.M., *Acta Cryst.* **2015**, *C*71, 3-8.
- 4. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J; Howard, J.A.K; Puschmann, H. J. *Appl. Cryst.* **2009**, 42, 339-341.
- 5. Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A.,

Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery Jr. J. A., Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Keith, T., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Rega, N., Millam, J. M., Klene, M. J., Knox, E., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Martin, R. L., Morokuma, K., Zakrzewski, V. G., Voth, G. A., Salvador, P., Dannenberg, J. J., Dapprich, S., Daniels, A. D., Farkas, O., Foresman, J. B., Ortiz, J. V., Cioslowski J., Fox, Gaussian 09, Revision D. 01, Gaussian, Inc., Wallingford CT, **2010**.

- 6. Reed, A. E., Weinstock, R. B., Weinhold, F., J. Chem. Phys., 1985, 83, 735-746.
- 7. Lu, T., Chen, F. W., J. Comp. Chem. 2012, 33, 580-592.
- 8. Humphrey, W., Dalke, A., Schulten, K. 1996, J. Mol. Graph., 14, 27-38.