Inorganic Chemistry

Communication

Synthesis of Ge$_2$NiS$_4$ Clusters and the Thermal Transformation to a Ge$_4$Ni$_6$S$_{12}$ Cluster

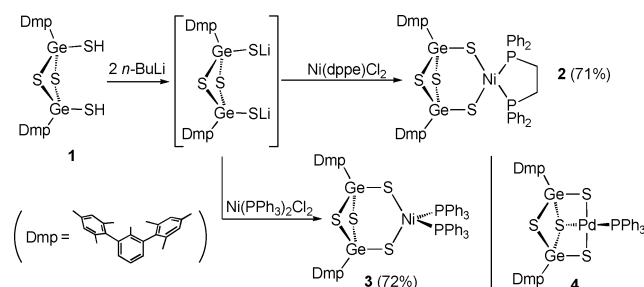**Tsuyoshi Matsumoto**, **Yosuke Matsui**, **Mikinao Ito**, and **Kazuyuki Tatsumi***

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The reaction of Ni(dppe)Cl$_2$ and *syn*-[DmpGe(SLi)(μ-S)$_2$Ge(SLi)Dmp] prepared in situ from *syn*-[DmpGe(SH)(μ-S)$_2$Ge(SH)Dmp] (**1**) and *n*-BuLi (2 equiv) afforded the Ge$_2$NiS$_4$ cluster, [DmpGe(μ-S)]$_2$(μ-S)$_2$Ni(dppe) (**2**) (Dmp = 2,6-dimesitylphenyl). The nickel in **2** assumes a slightly distorted square planar geometry. However, another Ge$_2$NiS$_4$ cluster, [DmpGe(μ-S)]$_2$(μ-S)$_2$Ni(PPh$_3$)$_2$ (**3**) obtained from a similar reaction with Ni(PPh$_3$)$_2$Cl$_2$, contains the nickel in a tetrahedron. When **3** was heated to 120 °C in toluene, a novel Ge$_4$Ni$_6$S$_{12}$ cluster [DmpGe(μ-S)$_3$]$_4$Ni$_6$ (**5**) was obtained. In cluster **5**, six nickels form an octahedron with the nickels occupying its vertexes, and four DmpGeS$_3$ units cap half of the trigonal faces.

Scheme 1

Metal chalcogenido clusters have attracted attention because of their versatile reactivities in relation to metalloenzymes[1] and industrial catalysts of hydrodesulfurization.[2] We have been especially interested in heteropolynuclear complexes composed of germanium and transition metals, anticipating their cooperation in reactions. Indeed, in our studies on S/S and S/O bridged heterodinuclear Ge–Ru complexes, the interaction of Ge and Ru was suggested in their structural changes upon alkylation and protonation of at the μ-S and μ-O.[3] Recently, we have synthesized a new dinuclear mercaptogermane *syn*-[DmpGe(SH)(μ-S)$_2$Ge(SH)Dmp] (**1**) as a building unit for germanium-containing metal clusters, and it was applied for the synthesis of Ge$_2$PdS$_4$ clusters.[4] Herein we report the synthesis of Ge/Ni/S clusters using **1**, which have different structural properties from the Pd analogues.

The reaction of Ni(dppe)Cl$_2$ and [DmpGe(SLi)(μ-S)$_2$Ge(SLi)Dmp] prepared in situ from **1** and 2 equiv of *n*-BuLi in THF afforded the Ge$_2$NiS$_4$ cluster, [DmpGe(μ-S)]$_2$(μ-S)$_2$Ni(dppe) (**2**), in 71% yield as brown crystals (Scheme 1). The ^{1}H NMR spectrum of **2** is in accordance with the structure, and the sharpness of the signals indicates its diamagnetism. X-Ray structural analysis reveals that the nickel sits in a slightly distorted square plane composed of the two germanethiolato sulfurs and dppe as shown in Figure 1.[5] The planar geometry about the nickel is incarnated in the sum of the bond angles around the Ni, 362.6°, which includes a large bite angle at S(3)–Ni(1)–S(4) (Table 1). This structure compares well with that of the palladium analogue which we have reported recently.[4]

A similar Ge$_2$NiS$_4$ cluster, [DmpGe(μ-S)]$_2$(μ-S)$_2$Ni(PPh$_3$)$_2$ (**3**), results from the reaction with Ni(PPh$_3$)$_2$Cl$_2$ as green crystals. Here the Ni(II) center resides in a tetrahedral geometry as shown in Figure 2, and the geometry with its associated paramagnetism is compatible with the broad signals observed in the ^{1}H NMR spectrum.

The Ge$_2$NiS$_4$ core has C_{2v} local symmetry, and the C_2 axis passes through the Ni(1) and the midpoint of Ge(1) and Ge(2). Because of the greater steric congestion derived from the bulk of PPh$_3$ ligands, the nickel in **3** assumes a tetrahedral geometry, which is allowed by the flexible dithiadigermet-

(1) (a) *Transition Metal Sulfur Chemistry, Biological and Industrial Significance*; Steifel, E. I., Matsumoto K., Eds.; American Chemical Society: Washington, DC, 1996. (b) *Transition Metal Sulphides–Chemistry and Catalysis*; Weber, Th., Prons, R., van Santen, R. A., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1998.

(2) (a) Topsøe, H.; Clausen, B. S.; Massoth, F. E. *Hydrotreating Catalysis: Science and Technology*; Springer-Verlag: Berlin, 1996. (b) Kabe, T.; Ishihara, A.; Qian, W. *Hydrodesulfurization and Hydrodenitrogenation: Chemistry and Engineering*; Kondasa-Wiley-VCH: Tokyo, 1999.

(3) (a) Matsumoto, T.; Nakaya, Y.; Itakura, N.; Tatsumi, K. *J. Am. Chem. Soc.* In press. (b) Matsumoto, T.; Nakaya, Y.; Tatsumi, K. *Angew. Chem., Int. Ed.* In press. (c) Matsumoto, T.; Nakaya, Y.; Tatsumi, K. *Organometallics* **2006**, *25*, 4835.

(4) Matsumoto, T.; Matsui, Y.; Ito, M.; Tatsumi, K. *Chem. Asian J.* In press.
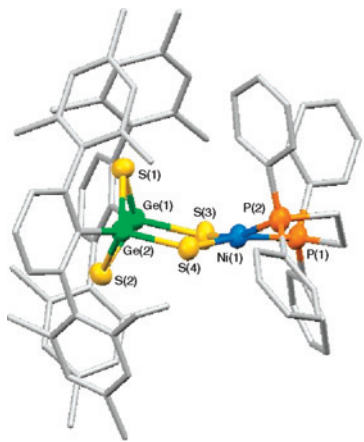
Figure 1. Molecular structure of **2**. All hydrogen atoms are excluded for clarity.
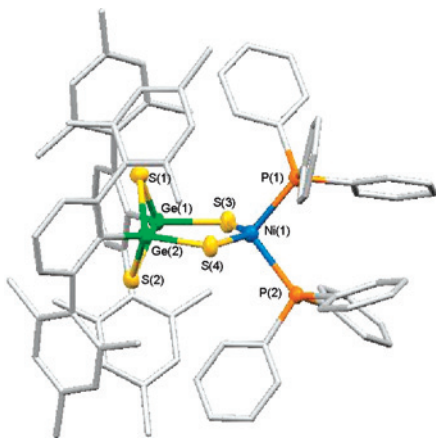
Figure 2. Molecular structure of **3**. All hydrogen atoms and the crystalline solvent molecules are excluded for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **2** and **3**

	2	**3**
Ge(1)–S(1)	2.2424(13)	2.2398(19)
Ge(1)–S(2)	2.232(2)	2.2483(18)
Ge(2)–S(1)	2.245(2)	2.258(2)
Ge(2)–S(2)	2.2342(13)	2.2559(18)
Ge(1)–S(3)	2.1808(13)	2.202(2)
Ge(2)−S(4)	2.1884(11)	2.187(2)
Ni(1)–S(3)	2.2226(15)	2.2614(17)
Ni(1)–S(4)	2.231(2)	2.2643(15)
Ni(1)–P(1)	2.172(2)	2.340(2)
Ni(1)–P(2)	2.1656(13)	2.357(2)
S(3)···S(4)	3.633(2)	4.079(2)
S(3)−Ni(1)−S(4)	109.33(6)	128.66(8)
S(3)−Ni(1)−P(1)	82.89(6)	109.75(7)
S(3)−Ni(1)−P(2)	162.71(9)	108.50(7)
S(4)−Ni(1)−P(1)	164.36(6)	103.03(6)
S(4)−Ni(1)−P(2)	82.86(6)	100.95(7)
P(1)−Ni(1)−P(2)	87.55(6)	103.09(8)
dihedral[a]	140.6	143.0

[a] Dihedral angles between planes Ge(1)−S(1)−S(2) and Ge(2)−S(1)−S(2).

anedithiolate property. Indeed, the S(3)−Ni(1)−S(4) bond angle for **3** becomes considerably larger than that for **2**, and the S(3)···S(4) distance of **3** is elongated accordingly by 0.45 Å from that of **2** (Table 1). Of note is the fact that the structure of **3** is completely different from that of the Ge_2PdS_4 cluster **4** (Scheme 1) obtained from the analogous reaction using $Pd(PPh_3)_2Cl_2$. Whereas the dithiadigermanedithiolate

coordinates to the Ni in **3** at the two germanethiolato sulfurs, it coordinates to the Pd in **4** at the three sulfurs including a μ-sulfide of the Ge_2S_2 quadrangle, in addition to the two thiolate sulfurs, to form a highly distorted square planar geometry at the Pd. These results are understandable because Ni has a rather small energy difference between its square planar and tetrahedral geometries and are in agreement with the common findings that the palladium(II) favors a square-planar coordination environment, while the coordination environment in the complexes of nickel(II) is much more variable.[6]

When cluster **3** was heated to 110 °C for 12 h, a slow color change from green to dark brown was observed. Separation of the crude products by preparative gel permeation chromatography (GPC) gave a major fraction at a significantly short retention time compared with that of **1**, indicating the unexpected formation of large clusters.[7] The recrystallization of this fraction from CH_2Cl_2/EtOH afforded the novel $Ge_4Ni_6S_{12}$ cluster $[DmpGe(\mu\text{-}S)_3]_4Ni_6$ (**5**) as brown crystals in 53% yield.[8] As shown in Figure 3, the cluster is composed of six square planar Ni^{2+} and four tetrahedral $[DmpGeS_3]^{3-}$ units. The six nickels form an octahedron as shown by the dotted line with the nickels occupying its vertexes, and the four $DmpGeS_3$ units cap half of the trigonal faces. The intramolecular Ni–Ni distances ranging from 3.078(2) to 3.184(2) do not indicate their significant interactions. The mean values of Ni–S and Ge–S distances are

(5) Crystal data for **2**: $C_{74}H_{74}Ge_2NiP_2S_4$; monoclinic; $C2/c$ (No. 15); $a = 30.814(3)$ Å, $b = 21.9372(16)$ Å, $c = 30.454(3)$ Å; $\beta = 127.5838(18)°$, $V = 16311(3)$ Å^3; $Z = 8$; $T = 193$ K; $\lambda = 0.71073$ Å; $F(000) = 5632$; $\mu = 11.363$ cm^{-1}; $\rho_{calcd} = 1.105$ g cm^{-3}; 91 233 reflections ($2\theta < 55.0°$), 18 666 unique ($R_{int} = 0.093$); R1 = 0.0860 ($I > 2\sigma(I)$), wR2 = 0.2642 (all data); GOF (on F^2) = 1.367. Crystal data for **3**·1.5toluene: $C_{94.5}H_{92}Ge_2NiP_2S_4$; triclinic; $P\bar{1}$ (No. 2); $a = 14.0364(14)$ Å, $b = 18.010(3)$ Å, $c = 18.085(3)$ Å; $\alpha = 106.910(6)°$, $\beta = 107.7173(13)°$, $\gamma = 95.117(2)°$, $V = 4086.6(9)$ Å^3; $Z = 2$; $T = 193$ K; $\lambda = 0.71073$ Å; $F(000) = 1690$; $\mu = 11.459$ cm^{-1}; $\rho_{calcd} = 1.318$ g cm^{-3}; 47 524 reflections ($2\theta < 55.0°$), 18 477 unique ($R_{int} = 0.143$); R1 = 0.0711 ($I > 2\sigma(I)$), wR2 = 0.2050 (all data); GOF (on F^2) = 0.959. Crystal data for **5**·CH_2Cl_2: $C_{97}H_{100}Cl_2Ge_4Ni_6S_{12}$; monoclinic; $P2_1/n$ (No. 14); $a = 22.913(7)$ Å, $b = 16.604(4)$ Å, $c = 27.451(11)$ Å; $\beta = 101.493(10)°$, $V = 10234(6)$ Å^3; $Z = 4$; $T = 193$ K; $\lambda = 0.71073$ Å; $F(000) = 4816$; $\mu = 25.735$ cm^{-1}; $\rho_{calcd} = 1.534$ g cm^{-3}; 96 655 reflections ($2\theta < 55.0°$), 23 294 unique ($R_{int} = 0.123$); R1 = 0.1156 ($I > 2\sigma(I)$), wR2 = 0.3044 (all data); GOF (on F^2) = 1.257. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. All calculations were performed with a Rigaku/MSC CrystalStructure program package except for refinement which was performed using SHELX-97 by full-matrix least squares against F^2. Anisotropic refinement was applied to all non-hydrogen atoms. All the hydrogen atoms were put at calculated positions, except for those of the disordered crystalline solvent molecules, two toluenes for **3** and a dichloromethane for **5**.

(6) Cotton, F. A.; Wilkinson, G.; Murillo, G. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley & Sons: New York, 1999; pp 840–842..

(7) Preparative GPC was performed on a LC-908 instrument (Japan Analytical Industry, Co. Ltd) with a series of Jaigel 1H and 2H columns, using chloroform as the eluent with 3.5 mL min^{-1}. The fraction containing **5** was observed at 45 min retention time, while **1** has a significantly longer 49 min retention time.

(8) Synthesis of $[DmpGe(\mu\text{-}S)_3]_4Ni_6$ (**5**). A toluene solution of **3** (200 mg, 0.135 mmol) was heated for 12 h at 110 °C. The crude product was separated by GPC (CHCl$_3$, 3.5 mL/min) to give a fraction of 45 min retention time, which was further crystallized by EtOH/CH$_2$Cl$_2$ to give **5** (27 mg) as a red crystals. The yield calculated on the basis of nickels is 53%. ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 7.47$ (t, $J = 7.6$ Hz, 4H, p-CH of Dmp), 6.98 (s, 16H, m-CH of Mes), 6.97 (d, $J = 7.6$ Hz, 8H, m-CH of Dmp), 2.27 (s, 24H, p-CH$_3$ of Mes), 1.83 (s, 48H, o-CH$_3$ of Mes). Elemental analysis calcd (%) for $C_{96}H_{100}Ge_4Ni_6S_{12}$: C, 50.55; H, 4.42; S, 16.87. Found: C, 49.98; H, 4.02; S, 16.90.
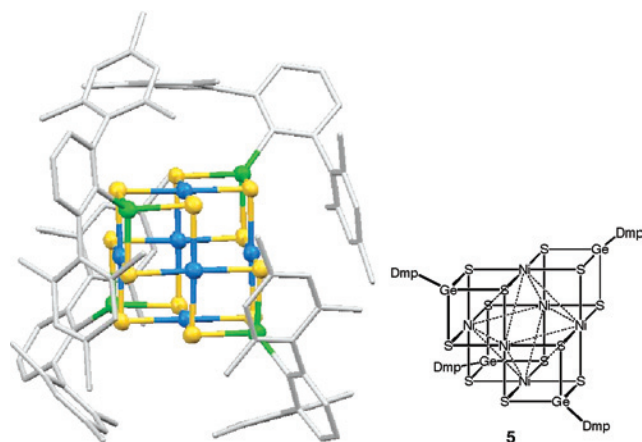
Figure 3. Molecular structure of **5** and its schematic structure. All hydrogen atoms and the crystalline solvent molecule are excluded for clarity. Color code: Ge, green; Ni, blue; S, yellow; C, gray.

2.249 Å (range 2.214(2) – 2.274(2) Å) and 2.222 Å (range 2.201(2) – 2.234(2) Å), which are ordinary values for those bonds, respectively.[9,10] The structure is consistent with the

diamagnetic properties indicated by the ^{1}H NMR spectra, which show a set of sharp signals assignable to the Dmp group.

In summary, new Ge/Ni/S clusters, [DmpGe(μ-S)]$_2$(μ-S)$_2$Ni(dppe) (**2**) and [DmpGe(μ-S)]$_2$(μ-S)$_2$Ni(PPh$_3$)$_2$ (**3**), were synthesized using the *syn*-[DmpGe(SH)(μ-S)$_2$Ge(SH)Dmp] (**1**) as a germanium source. Thermal transformation of **3** leads to a structurally unique Ge$_4$Ni$_6$S$_{12}$ cluster [DmpGe(μ-S)$_3$]$_4$Ni$_6$ (**5**). These results open a synthetic route to variegated sulfido clusters composed of germanium and transition metals.

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(10) Baines, K. M.; Stibbs, W. G. *Coord. Chem. Rev.* **1995**, *145*, 157.