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Facile Access to the Hydrazone Functionalized PdGeS Cluster $[\{R^NGe(\mu\text{-}S)_3\}_4Pd_6]$ from the Thiogermanate Anion $[\{R^NGe\}_2(\mu\text{-}S)_2S_2]^{2-}$

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The decanuclear ternary PdGeS cluster $[\{R^NGe(\mu\text{-}S)_3\}_4Pd_6]\cdot MeOH$ (**2**·MeOH) has been obtained in high yield by a two-step reaction, involving the derivatization of the carbonyl functionalized adamantane-like $[(R^1Ge)_4(\mu\text{-}S)_6]$ (R^1 = CMe_2CH_2COMe) with $N_2H_4\cdot H_2O$, and a subsequent reaction of the resulting hydrazone functionalized thiogermanate $(NH_3NH_2)_2[(R^NGe)_2(\mu\text{-}S)_2S_2]$ (R^N=$CMe_2CH_2CMeNNH_2$, **1**) with an acidic solution of (N,N′-tmeda)$Pd(NO_3)_2$. Cluster **2** has an elegant molecular structure which can be viewed as an R^N ligated ensemble of four edge-sharing $[Pd_3GeS_3]$ defect hetercubanes that meet at an unoccupied center. Thus, the cluster consists of six square-planar coordinated Pd^{II} ions at the vertices of a regular octahedron with four faces capped by four $[R^NGeS_3]^{3-}$ units. The title compounds were structurally characterized by means of single-crystal X-ray diffraction as well as physical property measurements. Moreover, density functional theory calculations were performed to gain insight into the unique coordination situation of the hydrazone substituent.

Introduction

Metal chalcogenide clusters are of considerable interest because of their remarkable structural diversity and chemical and physical properties. These have attracted interest from a broad variety of research fields for more than two decades.[1,2] Several synthetic approaches to these compounds have been developed in recent years. In addition to purely inorganic synthetic routes,[1c,3] the introduction of organic ligands with a designed functionality has been shown to be a convenient way to prepare a variety of new clusters with specific properties.[4] For example, very recently, Tatsumi and co-workers reported the formation of polynuclear NiGeS and PdGeS complexes, by the reaction of a thiogermanate precursor $Li_2[\{DmpGe\}_2(\mu\text{-}S)_2S_2]$ containing the sterically demanding Dmp ligand (Dmp = 2,6-dimesitylphenyl) with Ni^{II} and Pd^{II} complexes such as $[M(dppe)Cl_2]$ (M = Ni, Pd).[5]

In the course of our recent investigations on the synthesis and reactivity of functionalized chalcogenidometallate cages of the general type $[(R^XT)_4(\mu\text{-}E)_6]$ (R^X: R^1 = CMe_2CH_2COMe, R^2 = CH_2CH_2COOH; T = Ge, Sn; E = S, Se, Te),[6,7] we have developed a facile approach to several hydrazone derivatives of functionalized T/E complexes by the reaction of the starting material with hydrazine compounds NH_2NHR (R = H, Ph), like $[(R^YGe)_4(\mu\text{-}E)_6]$ (R^Y = $CMe_2CH_2CMeNNHPh$).[7] Herein, we report the formation of the highly reactive hydrazinium salt of a hydrazone functionalized thiogermanate $(NH_3NH_2)_2[\{R^NGe\}_2(\mu\text{-}S)_2S_2]$ (R^N = $CMe_2CH_2CMeNNH_2$, **1**), which was synthesized by treatment of the adamantane-type complex $[(R^1Ge)_4(\mu\text{-}S)_6]$[7] with hydrazine hydrate, and the ensuing reaction of **1** with (N,N′-tmeda)$Pd(NO_3)_2$, resulting in the formation of the decanuclear ternary PdGeS cluster $[\{R^NGe(\mu\text{-}S)_3\}_4Pd_6]\cdot MeOH$ (**2**·MeOH). Compounds **1** and **2**·MeOH were characterized by spectroscopy, elemental analysis, and single-crystal X-ray diffraction. Additionally, quantum chemical investigations employing density functional theory (DFT) methods were performed in order to analyze the bonding situation in the cluster with a coordination number of five at the Ge atoms.

Experimental Section

General. All manipulations steps were performed under an Ar atmosphere, unless otherwise noted. All solvents were dried and freshly distilled prior to use. Water was degassed by applying a dynamic vacuum (10^{-3} mbar) for several hours.

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(N,N′-tmeda)$PdCl_2$,[8] (N,N′-tmeda)$Pd(NO_3)_2$,[9] and $(CMe_2CH_2COMe)_4Ge_4S_6$[7] were prepared according to the reported methods. Pure $N_2H_4 \cdot H_2O$ and $Na_2S \cdot 9H_2O$ were purchased from Aldrich (> 98%) and used as received. ^1H NMR and ^{13}C NMR measurements were carried out using a Bruker DRX 400 MHz spectrometer at 25 °C. The chemical shifts were quoted in parts per million relative to the residual protons of deuterated solvents. EDX analyses were performed using the Voyager 4.0 EDX device of Noran Instruments, coupled with an electron microscope, CamScan CS 4DV. Infrared (IR) spectra were recorded on a Bruker IFS 88 spectrometer. Mass spectrometry (MS) was performed using a Finnigan MAT 95S. Electron Stoss ionization (ITMS-ESI) spectra were obtained by using solvent as the carrier gas. UV−vis spectra were recorded on a Perkin-Elmer Cary 5000 UV/vis/NIR spectrometer in the range of 800−200 nm employing the double-beam technique. The samples were prepared as suspensions in Nujol oil between two quartz plates.

Synthesis of $(NH_3NH_2)_2[(R^NGe)_2(\mu\text{-}S)_2S_2]$ (1). Hydrazine hydrate (0.022 g, 0.44 mmol) was added to the solution of thiogermanate $[(R^1Ge)_4(\mu\text{-}S)_6]$[7] (0.1 g, 0.11 mmol) in dichloromethane (10 mL) at room temperature. After 3 min of stirring, the precipitate appeared. The product was filtered off after 2 h of stirring and dissolved in 10 mL of methanol. Colorless crystals of **1** were obtained by slow diffusion of diethyl ether into the methanol solution (1:1) of the product within one day. Yield: 0.045 g (0.08 mmol, 72.4%). Mp: 171 °C. Elem Anal. Calcd: C, 25.46; H, 6.41; N, 19.80; S, 22.66. Found: C, 25.46; H, 6.36; N, 19.86; S, 22.59. ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ 1.03 (s, 12H, Me_2C), 1.62 (s, 6H, Me), 2.35 ppm (s, 4H, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 17.36 (Me), 23.32 (Me_2), 37.96 (CH_2), 45.81 (GeC), 147.37 ppm (C=N). IR (Nujol oil between KBr windows): $\tilde{\nu}$ 3224.0 (w), 2953.3 (s), 2924.6 (s), 2854.7 (s), 2723.3 (w), 2705 (vw), 2674.8 (vw), 2618 (vw), 2572 (vw), 1585.5 (w), 1460.1 (m), 1377.1 (m), 1260.0 (w), 1093.5 (w), 1022.2 (w), 799.4 (w), 723.3 (w), 408.8 cm^{-1}(m).

Synthesis of $[\{R^NGe(\mu\text{-}S)_3\}_4Pd_6] \cdot MeOH$ (2·MeOH). A solution of (N,N′-tmeda)$Pd(NO_3)_2$ (0.05 g, 0.16 mmol) in water (10 mL), carefully adjusted to a pH of 2−3 by the addition of diluted nitric acid to avoid dimerization of the Pd complex, was added slowly to the solution of **1** (0.08 g, 0.16 mmol) in methanol (10 mL) at 20 °C. A yellow precipitate appeared during the addition, which turned orange at the end of the addition. The product was filtered off after 30 min of stirring and dried in vacuo. It was partially dissolved in hot methanol. Red crystals of **2**·MeOH were obtained by slow evaporation of the methanol within 3 days. Yield: 0.04 g (0.023 mmol, 85%; it was calculated on the basis of palladium). Elem Anal. Calcd: C, 16.69; H, 3.14; N, 6.23; S, 21.39. Found: C, 16.88; H, 2.95; N, 6.30; S, 21.63. ^1H NMR (400 MHz, MeOD-d_4, 25 °C): δ 1.10 (s, 12H, Me), 2.54 (s, 24H, Me_2C), 2.92 ppm (s, 8H, CH_2). IR (KBr): $\tilde{\nu}$ 3432.6 (w), 3327.9 (w), 2923.3 (s), 2853.0 (s), 1601.9 (m), 1456.1 (m), 1383.2 (m), 1364.7 (s), 1243.5 (w), 1212.0 (w), 1156.2 (m), 1111.7 (w), 1039.9 (w), 1001.8 (w), 864.9 (s), 826.6 (s), 659.8 (m), 537.6 (w), 419.6 cm^{-1} (m). ESI−MS, *m*/*z*: 1767 [(M − MeOH) + H^+].

X-Ray Structure Determination. Data were collected on a diffractometer equipped with a Stoe IPDS2T imaging plate detector system using graphite-monochromized Mo Kα radiation ($\lambda = 0.71073$ Å) at 100 K. Structure solution and refinement were performed by direct methods and full-matrix least-squares on F^2, respectively, using the ShelxTL software.[10] Final crystallographic data and values of R_1 and wR_2 are listed in Table 1. Relevant bond distances and angles are listed in Table S1 (Supporting Information).

Table 1. Crystallographic and Refinement Details of **1** and **2** at 100 K

compound	**1**	**2**·MeOH
empirical formula	$C_{12}H_{36}Ge_2N_8S_4$	$C_{25}H_{56}Ge_4N_8OPd_6S_{12}$
fw /g mol^{-1}	565.91	1798.26
cryst color and shape	colorless needle	red plate
cryst size /mm^3	0.45 × 0.09 × 0.06	0.18 × 0.15 × 0.05
radiation (λ/Å)	Mo Kα, 0.71073	Mo Kα, 0.71073
cryst syst	monoclinic	monoclinic
space group	*C*2/*c*	*P*2_1/*n*
a /Å	20.411(5)	11.994
b /Å	8.445(3)	18.081
c /Å	29.410(5)	23.356
β /deg	110.89(3)	94.50
V /$Å^3$	4736.0(2)	5049.4
Z	8	4
ρ_{calcd} /g cm^{-3}	1.59	2.36
μ(Mo Kα) /mm^{-1}	2.9	4.9
abs correction type	analytical	ψ-scan
min/max transmission	0.740/0.945	0.440/0.613
2θ range /deg	9.24−53.94	9.60−53.60
no. of measured reflns	14876	27778
R(int)	0.1269	0.0751
Ind. reflns/ind. reflns with ($I > 2\sigma(I)$)	4953/3981	10381/ 5977
no. of parameters	289	519
R_1 ($I > 2\sigma(I)$)/wR_2 (all data)	0.0609/0.1694	0.0607/0.1120
S (all data)	1.077	0.941
largest diff. peak/hole /e^- $Å^{-3}$	1.85/−1.58	1.87/−0.76

Methods of the Quantum Chemical Investigations. DFT[11] investigations were undertaken by means of the program system TURBOMOLE, version 5.10,[12] using the RIDFT program[13] with the Becke-Perdew 86 (BP86) functional[14] and the gridsize m3. Basis sets were of def2-TZVP quality (TZVP = triple-ζ valence plus polarization).[15] For consideration of relativistic effects as well as to reduce the computational effort, according core potentials have been employed for Pd atoms (ECP-28).[16] All calculations were performed without symmetry (C_1) for convergence into global minimum structures. Shared electron numbers were calculated by means of a population analysis based on occupation numbers (PABOON, Ahlrichs, and Ehrhardt) using the program Moloch implemented in Turbomole.

Results and Discussion

Syntheses. The highly reactive hydrazinium salt of the hydrazone functionalized thiogermanate anion $(NH_3NH_2)_2[\{R^NGe\}_2(\mu\text{-}S)_2S_2]$ ($R^N = CMe_2CH_2CMeNNH_2$, **1**) precipitates quantitatively upon an in situ treatment of the recently reported C=O functionalized thiogermanate complex $[(R^1Ge)_4(\mu\text{-}S)_6]$[7] ($R^1 = CMe_2CH_2COMe$) with an excess of hydrazine hydrate. An ensuing reaction of **1** with (N,N′-tmeda)$Pd(NO_3)_2$ leads to the formation of the decanuclear ternary PdGeS cluster $[\{R^NGe(\mu\text{-}S)_3\}_4Pd_6] \cdot MeOH$ (**2**·MeOH). A yellow-orange precipitate of **2**·MeOH appears after 5 min in

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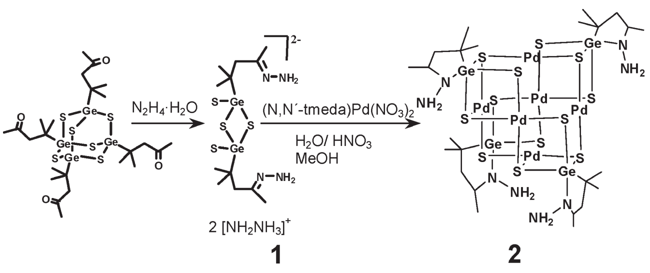
Scheme 1. Synthesis of Compounds **1** and **2** from $[(R^1Ge)_4(\mu\text{-}S)_6]$,[7] $N_2H_4 \cdot H_2O$, and (N,N′-tmeda)$Pd(NO_3)_2$



an almost quantitative yield. The two-step reaction is sketched in Scheme 1.

Crystal Structures. The anion of **1**, $[(R^NGe)_2(\mu\text{-}S)_2S_2]^{2-}$ (Figure 1), is formed by two S···S edge-linked R^NGeS_3 units, forming a slightly folded Ge_2S_2 four-membered ring (Ge1−S1−S2−Ge2, 165.04(2)°). Thus, it represents both a hydrazone derivative and a fragment of the starting material. A stoichiometric fragmentation of the starting material $[(R^1Ge)_4(\mu\text{-}S)_6]$ (R^1Ge/S = 2:3), which occurs during the formation of **1** (R^NGe/S = 1:2), releases 2 equiv of R^NGe/S per formula unit as a side product. A Ge/S atomic ratio of 1:1 in the side product was confirmed by EDX analyses of the residue upon removal of the filtrate solvent.

As is typical for dimeric chalcogenidotetrelate units, the Ge−(μ-S) bonds (Ge1−S1, 225.69(14); Ge2−S2, 225.78(14) pm) are longer than the Ge−S_t bonds (Ge1−S4, 213.57(16); Ge2−S3, 216.74(13) pm). The latter are clearly distinguished from those of Ge−SH units (233.1(2)−237.3(2) pm): whereas the latter are by about 20 pm longer, all reported Ge−S_t distances accord well to those in **1**, confirming its ionic nature.[17] However, the Raman spectrum shows a weak band at 2607 cm^{-1}, typical for S−H bonds, indicating some dynamic behavior of the protons of the hydrazonium group.[18] The folding of the central Ge_2S_2 ring is not observed in purely inorganic *pseudo*-D_{2h} symmetric $[Ge_2S_6]^{4-}$ anions, but it is typical for unsymmetric $R_2T_2E_4$ molecules.[19] The anion in **1** adopts pseudo-C_S symmetry.

In the molecular structure of **2** (Figure 2), four of the eight triangular faces of a nonbonded $[Pd^{II}]_6$ octahedron are capped by four $[R^NGeS_3]^{3-}$ units with the 12 S atoms bridging all octahedral edges. Alternatively, the cluster can be viewed as an R^N ligated ensemble of four $[Pd_3GeS_3]$ defect hetercubanes that each share three common edges with the three adjacent ones, leaving the center of the arrangement unoccupied. The pseudo-T_d symmetry of the ternary thiometallate core is, however, disturbed by the presence of the chelating CMe_2CH_2C-$MeNNH_2$ ligands.

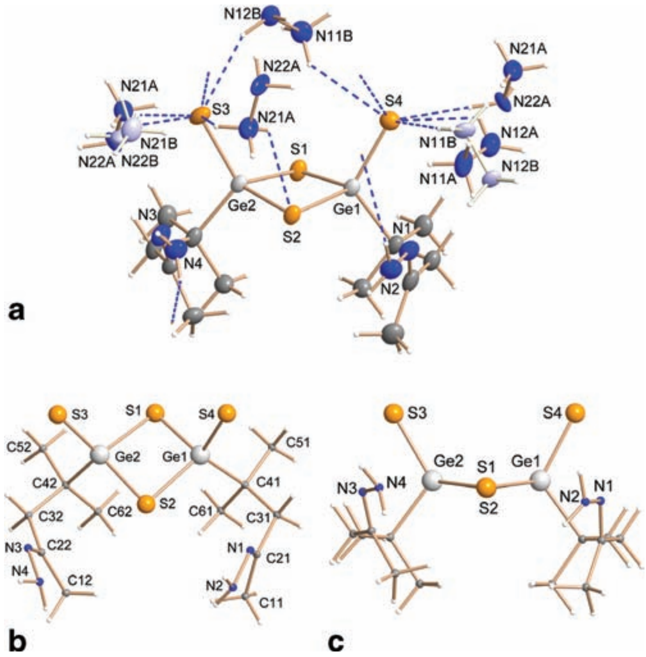


Figure 1. Molecular structure of compound **1**. (a) Thermal ellipsoid drawing (50% probability) of the asymmetric unit and further coordination of the anion to adjacent $[N_2H_5]^+$ cations. For clarity, disorder of the $[N_2H_5]^+$ cations is only shown once (dark and light blue representation, respectively). (b) Top and (c) side views of the anion. Selected distances (picometers) and angles (degrees): Ge−S(1,2), 225.69(14)−227.06(13); Ge−S(3,4), 213.57(16)−216.74(13); Ge−C, 197.5(5)−201.9(5); N(1,3)−N(2,4), 139.8(6)−140.2(6); N(11,21)−N(12,22), 140.3(13)−142.0(14); S1−Ge−S2, 95.28(5)−95.48(5); S(1,2)−Ge−S(4,3), 116.16(6)−116.57(6).

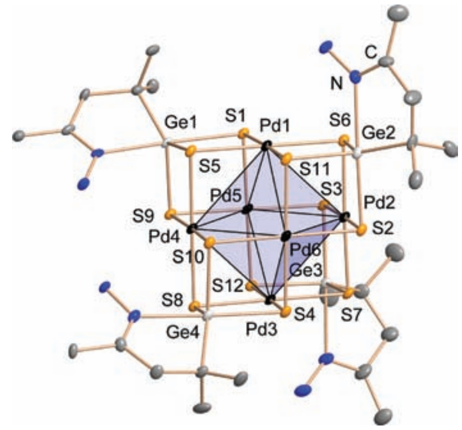


Figure 2. Thermal ellipsoid drawing (50% probability) of the molecular structure of **2**. H atoms are omitted for clarity. Selected distances (picometers) and angles (degrees): Pd−S, 232.0(3)−234.2(3); Ge−S(1−4), 235.4(3)−237.9(3); Ge−S(5−12), 223.1(3)−225.8(3); Ge−C, 198.6(10)−199.1(12); Ge−N, 220.7(9)−228.0(10); N−N, 138.0(11)−140.2(12); N−Ge−S(1−4), 174.3(2)−175.0(3); S−Ge−S, 87.36(10)−91.11(11); Ge−S−Pd, 85.68(10)−92.22(10).

The R^N-ligated PdGeS cluster core in **2** is topologically identical to the quoted, Dmp-shielded NiGeS cluster. Very similar topologies were observed in two further ternary clusters, the PR_3 ligated cation in $[Cu_4Nb_6Se_{12}O(PMe_3)_{10}]$-$[Cu_4NbSe_4Cl_2(PMe_3)_4] \cdot 1.5DMF$[20] and the purely

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inorganic M/Ge/Se anion in $[Ba_3(H_2O)_{15}][Mn_6(H_2O)_6(\mu_6\text{-}Se)(GeSe_4)_4]\cdot 9H_2O$.[21] In these compounds, the Nb or Mn atoms possess octahedral coordination, achieved by a central, μ_6-bridging Se ligand and additional ligands pointing away from the M_6 apexes, whereas in **2**, the d^8 configuration of the Pd^{II} centers leads to a preference of a square-planar coordination.

Unlike the situation in compound **1**, the terminal hydrazone groups of the organic ligands bind back to the Ge atoms in **2** to form a five-membered Ge−C−C−C−N ring. Thus, the Ge atoms adopt a trigonal-bipyramidal coordination. Furthermore, the Ge−S bonds trans to the coordinating N atom (237.4(3)−238.0(3) pm), which belong to the axial N−Ge−S arrangement in the trigonal bipyramid, are significantly longer than all other Ge−S bonds (224.5(3)−224.5(3) pm), which are in the common range for μ-S ligands. The mean value for the Pd−S bond length of 232.6 pm is in the same range as those of the known Pd^{II} complexes. The shortest Pd···Pd distances of 327.1 pm clearly exclude direct metal−metal bonding.[22] Interestingly, the orientations of the free NH_2 groups are different for the ligands at Ge1,4 versus Ge2,3: while the latter point toward different Pd atoms (Pd1 or Pd3, respectively), the former meet above the same vertex of the Pd_6 octahedron (Pd4). We assume that weak Pd···H interactions might support these arrangements, but it remains unclear whether the observed, unsymmetric arrangement is thermodynamically favored. Compound **2** does not show any crystallographic symmetry due to slight distortions but possesses a pseudo-C_2 axis through Pd2 and Pd4.

Optical Absorption Behavior. UV−visible spectra of **1** and **2**·MeOH (Figure 3) help to identify and discriminate the different charge transfer processes in **2**. A broad peak with a maximum at 2.73 eV (454 nm) can be assigned to the p(S) → d(Pd) charge transfer, according to similar values and similar band widths reported for further Pd/S complexes.[23] Another onset of absorption that is observed in two steps at 5.17 eV (240 nm) and 5.52 eV (225 nm) is due to p(S) → p(Ge) excitations in the asymmetric GeS_3 arrangement, as determined by comparison to the onset of absorption for **1** at 5.21 eV (238 nm).

Quantum Chemical Investigations. Simultaneous optimizations of the geometric and electronic structure of **2**, employing DFT[11] methods implemented in the program system Turbomole,[12] were helpful to illustrate the different Ge−S bonding situation at the Ge atom in the functionalized ternary cluster. Figure 4 shows the electron density in one of the molecular orbitals (MOs) of **2** that includes the Ge···N interaction. An anisotropic electron donation from the hydrazone N atom into an antibonding representation at the GeS_3 unit can be clearly seen and leads to the described anisotropic distortion.

The DFT method, which is the best one applicable to the given molecule, somewhat underestimates the weak Ge···N interaction: the calculated Ge−N distances are by 13 pm longer than the experimentally observed ones, and in turn the longer Ge−S(1−4) bonds trans to the latter are calculated by up to 1.5 pm as being too short. The remaining, shorter Ge−S(5−12) bonds show an elongation by 3−3.5 pm, as typical for DFT calculations. Population analyses based on occupation numbers[24] were performed on calculated **2** and several model compounds with different Ge···N contacts. According to the analyses, the elongated Ge−S(1−4) bonds contain about 85% of the electrons present in the shorter Ge−S(5−12) bonds. According to an extrapolation of the electron number for the calculated long Ge···N distance and the calculated values for several model compounds with different Ge−N bond lengths (see the Supporting Information), the bond strengths of the experimentally observed Ge···N interaction were estimated to amount to 32−43% of an ordinary Ge−N single bond at a coordination number four. Both results reflect the hypervalent situation at the Ge atoms that leads to weaker bonds throughout.

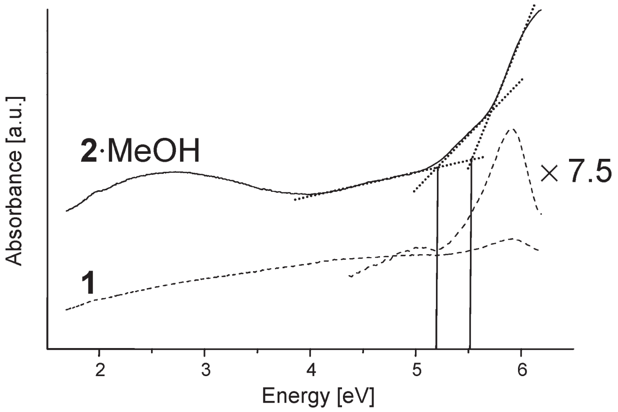

Figure 3. Solid-state UV−visible spectra of **1** (dashed line) and **2**·MeOH (solid line), recorded as suspensions of single crystals in nujol oil. The inset represents a zoom into the onset of absorption for **1** at 5.21 eV.

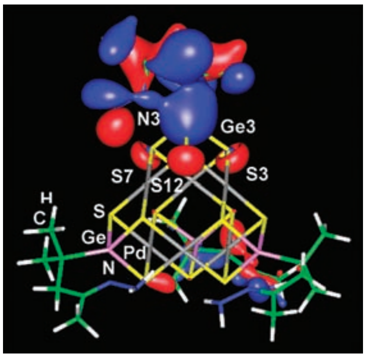

Figure 4. Illustration of the electron density (drawn to 0.2 e^{-} $Å^{-3}$) in one of the molecular orbitals that comprise the Ge···N interaction at Ge3 as an example of the five-coordinate Ge atoms. Selected distances (picometers) of the calculated molecule upon simultaneous optimization of electronic and geometric structure: Pd−S, 235.49−242.81; Ge−S(1−4), 235.14−236.36; Ge−S(5−12), 226.64−228.75; Ge−C, 204.23−204.68; Ge−N, 235.80−240.06; N−N, 137.36−137.51.

Besides the presence of 4d metal atoms, the nature of the ligand is the most significant difference seen in **2** compared to the related, Dmp-shielded NiGeS cluster.

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As can be seen from the molecular structures of **1** and **2**, and according to our previous investigations,[7] the hydrazone ligands can adopt either terminal or chelating coordination modes. Hence, they are rather flexible and may account for the individual requirements of the resulting complex, which is reflected, for instance, in an effective shielding of the cluster by the chelating ligands in **2**. Besides the kinetic effect, which is also observed for the bulky Dmp ligands in *syn*-$[\{DmpGe\}_2(\mu\text{-}S)_2(SH)_2]$,[5] the additional Ge···N contacts also provide some thermodynamic stabilization. As rationalized by the DFT investigations, each chelate ring provides an energy gain of 23.8−25.7 kJ mol^{-1}, that is, a total of about 100 kJ mol^{-1} for four rings in comparison with four open ligands—even for the somewhat too weak calculated interaction. Thus, the N → Ge back-bonding overcompensates the elongation and thus weakens the Ge−S bonds. As a consequence of the described stabilization, **2**·MeOH is not air-sensitive, and the molecular peak at 1766 *m*/*z* is observed in the ESI mass spectrum, which indicates the transfer of the complete cluster in the gas phase. The ^1H NMR data are consistent with the diamagnetic properties of **2**·MeOH, indicated by a set of sharp signals assignable to the R^N groups.

Another peculiarity of the ligands in **1** and **2** is the presence of both donor N atoms and free amine groups. For related thiostannate compounds comprising $SnCMe_2CH_2COMe$ units in a closed-ring manner,[7] it has been shown previously that chelating ligands of type R^1 or R^2 ($R^1 = CMe_2CH_2COMe$, $R^2 = C_2H_4COOH$) are readily opened in the presence of further transition metal ions. Thus, the coordination capability of the hydrazone N atoms and coupling reactions at the NH_2 groups with organic molecules of complementary functionality are currently under investigation.

Summary

In this report, we have presented the formation of a ternary, decanuclear PdGeS, $[\{R^NGe(\mu\text{-}S)_3\}_4Pd_6]$ ($R^N = CMe_2CH_2CMeNNH_2$), cluster from a preliminarily prepared, functionalized thiogermanate precursor, $(NH_3NH_2)_2[(R^NGe)_2(\mu\text{-}S)_2S_2]$. Beside an analogous, Dmp-shielded NiGeS cluster, the product represents the largest d^8-M/14/16 cluster known so far. The simple synthetic procedure, that is, the reaction of $(NH_3NH_2)_2[(R^NGe)_2(\mu\text{-}S)_2S_2]$ with (N,N′-tmeda)$Pd(NO_3)_2$, opens facile access to the synthesis of further M/14/16 clusters possessing a variety of reactive organic ligands. DFT investigations served to show that the presence of chelating, hydrazone-terminated ligands leads to an additional stabilization, which overcompensates the observed weakening of the Ge−S bonds at the five-coordinate Ge atoms.

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Supporting Information Available: CIF files for **1** and **2**·MeOH, selected bond lengths and bond angles, and ESI-mass spectra. This material is available free of charge via the Internet at http://pubs.acs.org.