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Varying Bonding Modes of the Zintl Ion $[Ge_9]^{4-}$ in Cu^I Complexes: Syntheses and Structures of $[Cu(\eta^4\text{-}Ge_9)(PR_3)]^{3-}$ (R = *i*Pr, Cy) and $[Cu(\eta^4\text{-}Ge_9)(\eta^1\text{-}Ge_9)]^{7-}$

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Three novel Cu-capped Ge_9 clusters were synthesized from K_4Ge_9 and phosphane-stabilized copper(I) compounds $CuCl(PR_3)$ with R = isopropyl (*i*Pr) or cyclohexyl (Cy). Reactions in *N*,*N*-dimethylformamide (dmf) at ambient temperature resulted in the isolation of $[Cu(\eta^4\text{-}Ge_9)(PCy_3)]^{3-}$ as a [K([2.2]crypt)] salt ([2.2]crypt: 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane). From solutions of $[Cu(\eta^4\text{-}Ge_9)(P\textit{i}Pr_3)]^{3-}$ in liquid ammonia, the anion was isolated when the reaction mixture was stored at –70 °C. Under the same reaction conditions but at a temperature of –40 °C the cluster $[Cu(\eta^4\text{-}Ge_9)(\eta^1\text{-}Ge_9)]^{7-}$ crystallized in the presence of [2.2.2]crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosan) or [2.2]crypt. The ligand-free intermetalloid cluster $[Cu(\eta^4\text{-}Ge_9)(\eta^1\text{-}Ge_9)]^{7-}$ is a unique example in which two differently bonded Ge_9 units are linked by a transition-metal atom. This cluster complex remarkably demonstrates the ability of homoatomic polyanions to bind in different modes to the same transition-metal atom. One Ge_9 *nido* cluster binds to the copper atom by means of its open square face, whereas the second Ge_9 *nido* cluster is coordinated through one lone pair as a two-electron σ donor. The key role of the flexible electron-donor properties of $[Ge_9]^{4-}$ in the reaction path towards the formation of intermetalliod clusters is discussed.

Introduction

The relationship between fullerenes and fullerides of carbon, and polyhedral anionic atom clusters of the heavier carbon congeners $[E_n]^{m-}$ (E = Si, Ge, Sn, and Pb) is corroborated by several findings. Alkylated species, oligomers, and polymers, as well as metal-encapsulating clusters, are known for both cage species.[1–4] Fullerides and Zintl anions have similar redox properties and both show electrostatic interactions with alkali metals in their salts.[5–7] Certainly, there are also intriguing differences. For instance, the stability of neutral species has been studied in depth for carbon fullerenes but only investigated in the gas phase for the heavier tetrel atom clusters. Endohedral anionic clusters of germanium, tin, and lead are more common and, in contrast to fullerenes, display an immense structural diversity; however, the mechanism of their formation has still not been sufficiently explored.[8,9] The nature of the chemical bonds in both species differs, even though similarities have been recognized here as well.[10,11] Whereas localized covalent single and double bonds are typical for fullerenes and fullerides, a concept of delocalized bonds is used for the description of polyhedral Zintl anions.

A further aspect in this analogy is the ability of the two cluster species to serve as ligands in transition-metal complexes. Several complex compounds are known for fullerides,[12] but only a few examples were reported for Zintl anions during the last decades.[8] Polyhedral nine-atom anions $[E_9]^{x-}$ (E = Si–Pb; x = 3, 4) react in two opposing ways with main-group elements and transition-metal compounds, respectively. Reactions of main-group-element compounds with tetrel-atom Zintl anions usually result in the addition of ligands to the cluster with formation of an *exo* bond,[9] but transition-metal compounds lead to capped, endohedrally filled, or capped endohedral clusters.[8] Fullerenes coordinate to transition-metal atoms through a double bond or in an η^5 fashion through a five-membered ring (Figure 1).[13,14] In contrast, the coordination of E_9 clusters to transition metals is so far limited to the open square face of the *nido*-shaped polyhedron, and only two examples in which a transition metal is coordinated in an η^5 fashion are known in the literature.[15,16]

The open square face of the *nido* E_9 polyhedron is isolobal to the cyclopentadienyl anion and to benzene, which are rather common six-electron donors in organometallic compounds. Thus, various transition-metal fragments appear suitable to build complexes with E_9 anions, but up to now the reactions have succeeded only for group 6, 9, 10, and 12 elements. First of all, the crystal structures of the complexes $[M(\eta^4\text{-}E_9)(CO)_3]^{4-}$ (E = Sn, Pb; M = Cr, Mo, W)[15–19] were reported, followed by compounds that contained isolobal fragments $[Zn(\eta^4\text{-}E_9)R]^{3-}$ (E = Si–Pb; R = Ph, *i*Pr, Mes).[20,21] Recently, the heavier group 12 homologue Cd was also added to E_9 clusters (E = Sn, Pb) and the coordinative E_9–Cd bond in $[Cd(\eta^4\text{-}E_9)(C_6H_5)]^{3-}$ turned out to be strong enough to endure a ligand exchange at the

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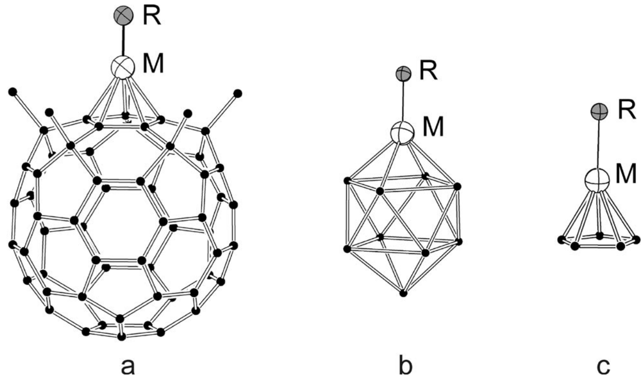

Figure 1. Transition-metal (M) complexes with a homoatomic polyhedron and rings acting as six-electron donor ligands. (a) $[M\{\eta^5\text{-}C_{60}(R')_5\}(\eta^1\text{-}R)]^{x-}$, (b) $[M(\eta^4\text{-}E_9)(\eta^1\text{-}R)]^{x-}$, and (c) $[M(\eta^5\text{-}C_5H_5)(\eta^1\text{-}R)]^{x-}$.

Cd atom to give the clusters $[Cd(\eta^4\text{-}E_9)(Sn_3)]^{3-}$.[22] Further, $[Ni(\eta^4\text{-}Ge_9)(CO)]^{3-}$ was presented as the only known paramagnetic E_9 cluster complex and the only example with a group 10 element in capping position to an empty *nido* E_9 cluster.[23] The synthesis of $[Ir(\eta^4\text{-}Sn_9)(cod)]^{3-}$ (cod = cyclooctadiene) currently proved that group 9 elements can also be coordinated to an E_9 cluster. In a subsequent reaction, the Ir atom is encapsulated into a Sn atom cage with formation of the larger cluster $[Ir@Sn_{12}]^{3-}$.[24]

Here we report on reactions of K_4Ge_9 with phosphane-stabilized Cu^I halides $Cu^ICl(PR_3)$ (R = *i*Pr, Cy) in dimethylformamide and liquid ammonia solution and under diverse conditions, which yielded three new copper-capped $[Ge_9]^{4-}$ clusters including the ligand-free, intermetalloid species $[Cu(\eta^4\text{-}Ge_9)(\eta^1\text{-}Ge_9)]^{7-}$. This cluster remarkably demonstrates for the first time the ability of homoatomic polyanions to bind in different modes to the same transition-metal atom. Such variations of donor properties might play a key role in the reaction path towards the formation of intermetalloid clusters.

Results

$[Cu(\eta^4\text{-}Ge_9)(PCy_3)]^{3-}$ (**1a**) was obtained from the reaction of $Cu^ICl(PCy_3)$ and K_4Ge_9 in dimethylformamide in the presence of [2.2]crypt as cation sequestering compound. The related cluster $[Cu(\eta^4\text{-}Ge_9)(P\textit{i}Pr_3)]^{3-}$ (**2a**) resulted as a [K([2.2.2]crypt)] salt from a solution of $Cu^ICl(P\textit{i}Pr_3)$ and K_4Ge_9 in liquid ammonia at –70 °C. At a temperature of –40 °C, $Cu^ICl(PR_3)$ led to the cluster $[Cu(\eta^4\text{-}Ge_9)(\eta^1\text{-}Ge_9)]^{7-}$ (**3a**) for both R = *i*Pr and Cy.

Compound **3** crystallizes in the triclinic space group $P\bar{1}$ with three [2.2]crypt-sequestered and four unsequestered K^+ cations per cluster anion (**3a**), as well as $21NH_3$ molecules. Replacement of [2.2]crypt by [2.2.2]crypt in the reaction mixture led to the compound $K_5[K([2.2.2]crypt)]_2[Cu(\eta^4\text{-}Ge_9)(\eta^1\text{-}Ge_9)](NH_3)_{14+x}$ (**4**), in which **3a** is counterbalanced by two $[K([2.2.2]crypt)]^+$ units and five unsequestered K^+ cations. The compound crystallizes in the triclinic crystal system with at least 14 ammonia molecules per formula unit.

Orange crystals of compound $[K([2.2]crypt)]_3[Cu(\eta^4\text{-}Ge_9)(PCy_3)](dmf)_{2.5}$ (**1**) were revealed to crystallize in the trigonal space group $P\bar{3}$ with six formula units per unit cell. Three $[K([2.2]crypt)]^+$ units were located per cluster, which thus carries a threefold negative charge.

Thus the anion $[Cu(\eta^4\text{-}Ge_9)(PCy_3)]^{3-}$ (**1a**, Figure 2) adopts the shape of a bicapped square antiprism, in which one capping vertex is occupied by a Cu atom coordinated by PCy_3. All Ge–Ge distances of **1a** fit well into the expected range of delocalized cluster bonds.[2,20,23,25] As in previously reported structures of transition-metal-capped *nido*-E_9 clusters,[15,19–21] the longest Ge–Ge contacts occur within the two square faces Ge2 to Ge5 [av. 2.815(2) Å] and Ge6 to Ge9 [av. 2.732(2) Å]; the square face adjacent to the transition metal is slightly smaller. The Ge–Ge bond lengths to the capping Ge1 lie in the range from 2.548(2) Å (Ge1–Ge2) to 2.586(2) Å (Ge1–Ge4) and are significantly longer than the corresponding Cu–Ge contacts [2.479(1)–2.497(1) Å]. For comparison the covalent radii of copper

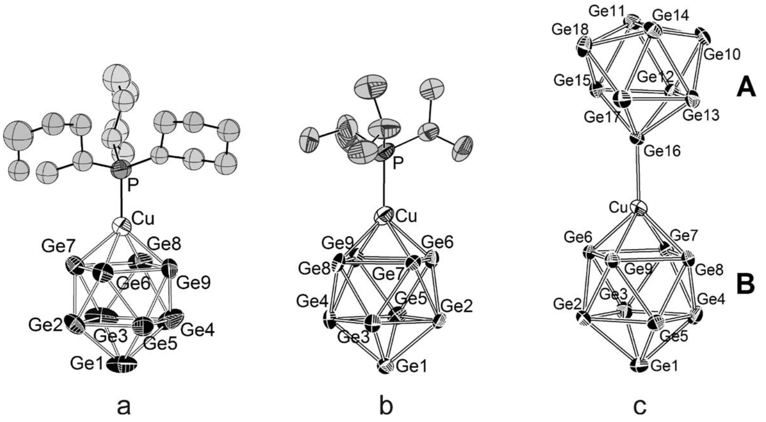

Figure 2. Copper-capped $[Ge_9]^{4-}$ clusters. All atoms are shown as ellipsoids at the 60% probability level. Carbon atoms are shown as gray ellipsoids. Hydrogen atoms are omitted for clarity. (a) $[Cu(\eta^4\text{-}Ge_9)(PCy_3)]^{3-}$ (**1a**), (b) $[Cu(\eta^4\text{-}Ge_9)(P\textit{i}Pr_3)]^{3-}$ (**2a**), and (c) $[Cu(\eta^4\text{-}Ge_9)(\eta^1\text{-}Ge_9)]^{7-}$ (**3a**).

and germanium are 1.38 and 1.22 Å, respectively.[26] The Cu–P distance in $[Cu(\eta^4\text{-}Ge_9)(PCy_3)]^{3-}$ is 2.225(2) Å and is slightly elongated relative to that in $Cu^ICl(Cy_3P)$ [2.183(2) Å].[27] Crystals of compound **1** were dissolved in dmf for ^{31}P NMR spectroscopy measurements. The investigations reveal that the phosphane ligand is easily separated from the copper atom in dmf, for in the ^{31}P NMR spectrum a sharp signal of noncoordinating PCy_3 (δ =10.3 ppm) is found next to a very broad signal at 6.7 ppm, which is generated by **1a**. The integral intensity of the PCy_3 peak increases with time.

Analogous reactions in dmf were carried out with $Cu^ICl(P\mathit{i}Pr_3)$ and in the presence of [2.2.2]crypt, [2.2]crypt, or [18]crown-6, but crystals were not obtained. ^{31}P NMR spectroscopy studies on the reaction solutions gave no evidence for the formation of a cluster complex similar to **1a**. Therefore the experiments were carried out in liquid ammonia solutions, from which orange crystals of $[K([2.2.2]crypt)]_3[Cu(\eta^4\text{-}Ge_9)(P\mathit{i}Pr_3)](NH_3)_{13}$ (**2**) were finally isolated at a temperature of –70 °C. Compound **2** crystallizes in the monoclinic crystal system with space group *C*2/*c* and eight formula units per unit cell. Each cluster $[Cu(\eta^4\text{-}Ge_9)(P\mathit{i}Pr_3)]^{3-}$ (**2a**, see Figure 2) is accompanied by three well-ordered $[K([2.2.2]crypt)]^+$ units. Cluster **2a** is a derivative of **1a** with the shape of a bicapped square antiprism and the Cu atom as one apex. Its Ge–Ge bond lengths are in accordance with known structures of Ge_9 fragments.[2,20,23,25] The long Ge–Ge contacts within the two square faces Ge2 to Ge5 [av. 2.814(1) Å] and Ge6 to Ge9 [av. 2.739(1) Å] are almost equal to the corresponding distances in **1a**, and the Cu-capped square is again slightly smaller. The bonds of capping atom Ge1 range from 2.562(1) Å (Ge1–Ge2) to 2.591(1) Å (Ge1–Ge3) and the equivalent Cu–Ge bonds are notably shorter [2.466(1)–2.522(1) Å]. The Cu–P distance in **2a** is 2.241(2) Å and therefore longer than in $Cu^ICl(P\mathit{i}Pr_3)$ (**7**) [2.1928(5) Å] but shorter than in $Cu^ICl(P\mathit{i}Pr_3)_2$ (**8**) [av. 2.2533(6)].[28]

At a temperature of –40 °C and in the presence of [2.2]crypt, the cluster $[Cu(\eta^4\text{-}Ge_9)(\eta^1\text{-}Ge_9)]^{7-}$ (**3a**, see Figure 2) was gained from a reaction of $Cu^ICl(PR_3)$ (R = Cy, *i*Pr) and K_4Ge_9 in liquid ammonia. The compound $K_4[K([2.2]crypt)]_3[Cu(\eta^4\text{-}Ge_9)(\eta^1\text{-}Ge_9)](NH_3)_{21}$ (**3**) crystallizes in the triclinic space group $P\bar{1}$ with two formula units per unit cell. A sevenfold negative charge can be deduced for **3a** according to four K^+ cations and three $[K([2.2.2]crypt)]^+$ units.

The anion $[Cu(\eta^4\text{-}Ge_9)(\eta^1\text{-}Ge_9)]^{7-}$ consists of two clusters, one of which (**A**) adopts the shape of a bicapped square antiprism, as found for **1a** and **2a** with a Cu atom in the capping position to a *nido*-Ge_9 cage. A further C_{4v}-symmetric Ge_9 cluster (**B**) coordinates with one Ge atom of the open square face of the cluster to the Cu atom, and thus a cluster *exo* contact is established by means of a two-electron σ-donor bond of Ge (lone pair). All bond lengths in **3a** compare well with previously reported naked and derivatized Ge_9 clusters.[2,20,23,25] Similar to **1a** and **2a**, the mean distances to the capping Ge atoms are 2.571(1) Å in cluster **A** and 2.574(1) Å in cluster **B**, and the Cu–Ge contacts in **A** are 2.501(1) Å on average. The mean Ge–Ge contacts within the Ge-capped square faces are almost equal for Ge2 to Ge5 in cluster **A** [av. 2.823(1) Å] and Ge11 to Ge15 in cluster **B** [av. 2.820(1) Å]. As in **1a** and **2a**, the Cu-capped square face is somewhat smaller [av. 2.729(1) Å]. The equivalent distances from Ge15 to Ge18 in cluster **B** are significantly shorter [av. 2.580(1) Å]. The atom Ge16 binds with its lone pair to the Cu atom. As a consequence, the contacts Ge16–Ge15 and Ge16–Ge17 are reduced to 2.551(1) and 2.556(1) Å, respectively, as was reported already for other Ge_9 clusters with *exo* bonds.[9] Nevertheless, the ratio of the two diameters of the open square face in **B** is equal to 1.00 and its torsion angle is 175.69(5) Å. As expected for a more localized bond, the Cu–Ge16 *exo* contact [2.362(1) Å] is considerably shorter than the Cu–Ge bonds in cluster **A**, **1a**, and **2a**.

In all previously reported isolobal transition-metal complexes of *nido*-$[Ge_9]^{4-}$ clusters with $2n + 2 = 22$ skeleton electrons, the heteroatom possesses a d^{10} electron configuration.[8,9] For cluster **1a**, ^{31}P NMR spectroscopy measurements of solutions of **1** reveal a diamagnetic complex with the Cu atom having a closed d^{10} electron system and thus the formal charge of +1. The same might hold true for **2a** and **3a**. Organometallic M(**L**) fragments with a two-electron donor **L** and a d^{10} transition-metal M are isolobal to $H\text{–}B^{2+}$ or $H\text{–}C^{3+}$ that comprise unoccupied s and p orbitals available for cluster bonding. Thus by the addition of a $Cu(\mathbf{L})^+$ fragment (**L** = PR_3 or $\eta^1\text{-}Ge_9{}^{4-}$) to the *nido*-$[Ge_9]^{4-}$ cluster, it converts to a ten-vertices *closo* cluster with D_{4d} symmetry. The threefold negative charge of **1a** and **2a** arises from a $[Ge_9]^{4-}$ cluster capped by a copper(I) atom that does not provide electrons for cluster framework bonding. A similar charge allocation can be supposed for cluster **A** in **3a**. The Ge_9 cluster **B** of **3a** acts as two-electron donor and features the same donor properties as the very common PR_3 ligands. For **3a**, an overall charge of –7 results. Alternatively, the stability of the complexes **1a** to **3a** can also be explained by the 18-electron valence shell of Cu^I. A σ-donor ligand **L** (**1a**, **2a**: **L** = phosphane; **3a**: **L** = $[Ge_9]^{4-}$) supplies two electrons (lone pair), and the *nido*-type $[Ge_9]^{4-}$ cluster provides six electrons of the frontier orbitals localized at the atoms of the open square face to complete the Cu valence shell. Indeed, several isolobal copper complex compounds of the general formula $[Cu(C_5H_5)(PR_3)]$ (Figure 1c) are reported in the literature.[29,30]

The anions of compound **1a** and **3a** are closely surrounded by potassium cations. The cluster **1a** interacts electrostatically with two $[K([2.2]crypt)]^+$ units; in a more detailed explanation, K1 coordinates to an edge of the waist of **1a** and K2 coordinates to one bond of the capping Ge atom (see Figure 3). The K–Ge distances are 3.500(4) and 3.907(3) Å for K1 and 3.508(3) and 4.024(3) Å for K2. K3 instead has one longer contact to Ge7 in **1a** [4.231(3) Å] and is additionally coordinated by one solvent molecule that is situated between the cluster and the $[K([2.2]crypt)]^+$ unit. The Cu–Ge16 contact in cluster **3a** is encircled by an almost planar square of four potassium atoms, K1 to K4, perpendicularly to the contact between **A** and **B** (Figure 3).

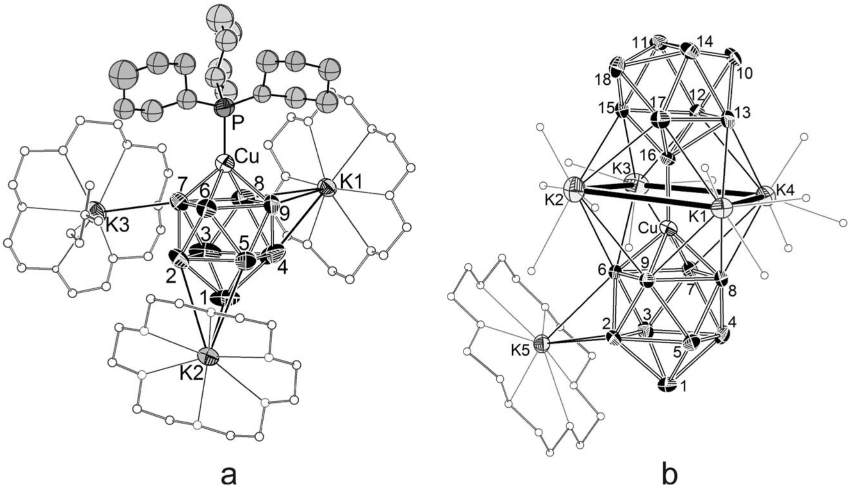

Figure 3. Structure of (a) $[Cu(\eta^4\text{-}Ge_9)(PCy_3)]^{3-}$ (**1a**) and (b) $[Cu(\eta^4\text{-}Ge_9)(\eta^1\text{-}Ge_9)]^{7-}$ (**3a**) with their coordinating potassium atoms. Heavy atoms are shown anisotropically with 60% occupation probability. For clarity, hydrogen atoms are omitted and the atoms in cryptand and solvent molecules are shown as empty spheres. Germanium atoms are identified by their atom number.

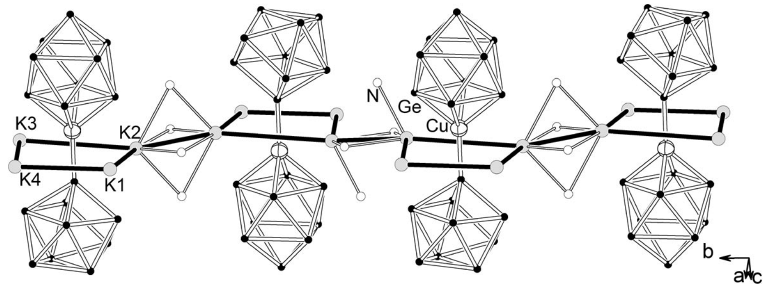

Figure 4. Chain along the crystallographic *b* axis in $K_4[K([2.2]crypt)]_3[Cu(\eta^4\text{-}Ge_9)(\eta^1\text{-}Ge_9)](NH_3)_{21}$ (**3**). All K (except K5) and Ge atoms are shown as well as the nitrogen atoms of the bridging NH_3 molecules. Lines between the K atoms do not represent bonds but serve as a guide for the eye.

Similar cation arrangements due to electrostatic interactions were found for Ge_9 dimers as well.[31] In **3a** the K–Ge distances are between 3.418(2) Å (Ge15–K3) and 3.978(2) Å (Ge15–K2), and the K–K contacts within this square face range from 4.268(3) Å (K1–K4) to 5.245(3) Å (K1–K2). The torsion angle of the plane of K1 to K4 is 175.51(6)°. The potassium atoms are stabilized by ammonia molecules, and K2 and K3 build four and two ammonia bridges to their symmetry equivalents K2* and K3*, respectively. Therefore the shortest contacts occur between K2 and K2* [3.646(4) Å] as well as K3 and K3* [3.731(4) Å], and a one-dimensional chain $^1_\infty\{[K_4\{Cu(\eta^4\text{-}Ge_9)(\eta^1\text{-}Ge_9)\}]^{3-}\}$ as shown in Figure 4 develops in the direction of the *b* axis. All the K atoms of one chain are in-plane. Further, the [2.2]crypt-sequestered K5 coordinates to **3a** by means of the triangular face Ge2–Ge3–Ge6 of the waist of cluster **A** through three short contacts [av. 3.658(2) Å]. The remaining two potassium atoms are completely separated from the anionic cluster, and each coordinates to one [2.2]-crypt molecule and two ammonia molecules.

Discussion

The ability of $[Ge_9]^{4-}$ to form *exo* σ bonds to transition-metal atoms has already been demonstrated in a few compounds: As a first example, the anionic polymer $^1_\infty\{(Hg\text{-}Ge_9)^{2-}\}$ (**5a**) was described in which Hg atoms are covalently bonded to Ge_9 clusters (Figure 5, a).[32,33] However, in **5a** each Hg atom forms two further short coordinative contacts to Ge atoms of the cluster under consideration. The previously reported reaction of K_4Ge_9 and $Au^ICl(PPh_3)$, which is an analogue of the Cu compounds used in this investigation, yielded the cluster $[(\mu^2\text{-}Au)_3(\eta^3\text{-}Ge_9)_2]^{5-}$ (**6a**).[34] Anion **6a** was isolated as a [K([2.2.2]crypt)] salt from an ethylenediamine solution at ambient temperature. In **6a**, an equilateral triangle of three Au atoms stabilized by aurophilic interactions[35] bridges two Ge_9 clusters in a parallel face-to-face arrangement (Figure 5, b). Each Au atom is linearly coordinated by two Ge atoms, which is certainly the preferred orientation for Au^I. To the contrary, in the cluster $[Au_3Ge_{45}]^{9-}$, which was obtained from the same reaction mixture by changing the reaction conditions, each of the three Au atoms coordinates to four Ge atoms in a rectangular-planar fashion. Theoretical investigations showed that the Au atoms are best described with formal oxidation state +I.[36]

The Cu atom in **3a** tends to reach 18 valence electrons and interconnects two Ge_9 cages, one of which acts as six-electron π donor, whereas the second Ge_9 cage provides a distinct lone-pair donor bond. In the case of deltahedral

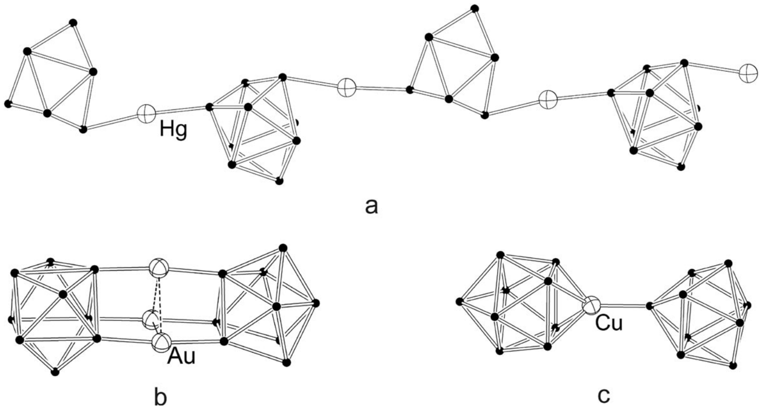

Figure 5. Comparison of ligand-free Ge_9 clusters with σ-bonded transition-metal atoms. (a) $^1\{_\infty[(HgGe_9)^{2-}]\}$ (**4a**), (b) $[(\mu^2\text{-}Au)_3(\eta^3\text{-}Ge_9)_2]^{5-}$ (**5a**), and (c) $[Cu(\eta^4\text{-}Ge_9)(\eta^1\text{-}Ge_9)]^{7-}$ (**3a**).

clusters, the latter coordination was solely reported for the ligand-stabilized octahedral anions $[\{EM(CO)_5\}_6]^{2-}$ (E = Ge, Sn; M = Cr, Mo, W)[37] with an underlying $[E_6]^{2-}$ octahedron and for the recently described functionalized *nido*-Ge_9 core in $\{Ge_9[Si(SiMe_3)_3]_3Cr(CO)_5\}^-$.[38]

The comprehensive investigation of the reactivity of $[Ge_9]^{4-}$ solutions towards $Cu^ICl(PR_3)$ (R = *i*Pr, Cy) revealed that the ligand substitution at the Cu atom occurs stepwise. In the anions **1a** and **2a**, the labile Cl^- is replaced by a $[Ge_9]^{4-}$ cluster that coordinates in an η^4 fashion. The more stable copper(I)–phosphane bond is broken only in liquid ammonia at a temperature of –40 °C, and the cluster **3a** forms.

In summary, the formation of cluster **3a** through **1a** shows the stepwise formation of intermetalloid clusters. Similar results were recently reported for the formation of cluster $[Ir@Sn_{12}]^{3-}$.[24] The inclusion of the Ir metal occurs through the formation of the complex $[Ir(\eta^4\text{-}Sn_9)(cod)]^{3-}$, which transforms under oxidation to $[Ir@Sn_{12}]^{3-}$. Compound **3a** now presents the missing link on how cluster growth takes place: the second cluster approaches the transition metal by means of a ligand-exchange reaction.

Experimental Section

Syntheses: All manipulations were carried out under a purified argon atmosphere using standard Schlenk-line and glove-box techniques. K_4Ge_9 was prepared by fusion of stoichiometric amounts of the elements in stainless steel tubes at 650 °C. Dimethylformamide (Merck) was distilled from calcium hydride and used immediately after collection. Liquid ammonia was dried and stored with sodium metal. Toluene was dried in a solvent purification system (MBraun). [2.2]Crypt and [2.2.2]crypt (Merck) were dried in vacuo for eight hours. (Tricyclohexylphosphane)copper(I) chloride and (triisopropylphosphane)copper(I) chloride were prepared according to the literature.[39,40]

For the preparation of $[K([2.2]crypt)]_3[Cu(\eta^4\text{-}Ge_9)(PCy_3)](dmf)_{2.5}$ (**1**), a mixture of K_4Ge_9 (0.15 mmol), $CuCl(PCy_3)$ (0.15 mmol), and [2.2]crypt (0.380 mmol) was dissolved in dimethylformamide (2 mL) and stirred for two hours. The intense dark brown to green solution was separated from the residue by filtration and carefully layered with toluene (2 mL). Compound **1** crystallized after three days at –25 °C as orange hexagonal columns. Yield 46%. $C_{61.5}H_{128.5}CuGe_9K_3N_{8.5}O_{14.5}P$ (2084.35): calcd. C 35.4, H 6.2, N 5.7, P 1.5, Ge 31.3, Cu 3.0; found C 34.8, H 6.47, N 4.41, P 1.8, Ge 28.3, Cu 2.8. Small differences in expected composition are attributed to disordered solvent molecules in crystals of **1** (see the section on Structure Determination below) and to the disruption of the presence of phosphorus to photometrical determination of the Ge content. ^{31}P NMR: δ = 6.71 ppm.

$[K([2.2.2]crypt)]_3[Cu(\eta^4\text{-}Ge_9)(P\mathit{i}Pr_3)](NH_3)_{13}$ (**2**) was obtained from a dark red solution of K_4Ge_9 (0.15 mmol), $CuCl(P\mathit{i}Pr_3)$ (0.15 mmol), and [2.2.2]crypt (0.266 mmol) in liquid ammonia. The solid starting materials were weighed together and dissolved in ammonia (ca. 2 mL) at –78 °C. The solution was kept at –70 °C until **2** crystallized after two months.

The compound $K_4[K([2.2]crypt)]_3[Cu(\eta^4\text{-}Ge_9)(\eta^1\text{-}Ge_9)](NH_3)_{21}$ (**3**) was synthesized from K_4Ge_9 (0.15 mmol), $CuCl(PR_3)$ (0.15 mmol; R = *i*Pr, Cy), and [2.2]crypt (0.380 mmol) by the addition of liquid ammonia (ca. 2 mL) to the solid starting materials at –78 °C. After storing the dark red solution at –40 °C for one month, orange crystalline prisms of **3** had formed.

For the synthesis of compound $K_5[K([2.2.2]crypt)]_2[Cu(\eta^4\text{-}Ge_9)(\eta^1\text{-}Ge_9)](NH_3)_{14+x}$ (**4**), K_4Ge_9 (0.15 mmol), $CuCl(PR_3)$ (0.15 mmol; R = *i*Pr, Cy), and [2.2.2]crypt (0.266 mmol) were weighed together and dissolved in liquid ammonia (ca. 2 mL) at –78 °C. At a temperature of –40 °C, **4** was yielded as small orange crystals after three weeks.

Structure Determination: A suitable crystal of compound **1** was selected from under perfluoropoly(alkyl ether) inside a glove box. The crystals of compounds **2**, **3**, and **4** are thermally very unstable and sensitive to air and moisture. They were transferred out of the mother liquor into perfluorpoly(alkyl ether) oil at 213 K under a cold stream of N_2 gas. For the crystal-structure analysis, single crystals of the compounds were fixed on glass capillaries and positioned in a cold N_2 stream using the crystal cap system for the ammoniats **2**, **3**, and **4**. The data sets were collected with an Oxford Diffraction Xcalibur3 diffractometer, Mo-K_α radiation (λ = 0.71073 Å) at 150(2) K (**1**) and 120(2) K (**2**, **3**), respectively. The structures were solved by direct methods and refined by full-matrix least-squares calculations against F^2 using the SHELXTL V6.1 package.[41] The positions of the hydrogen atoms were geometrically determined in all crystal structures and refined using a riding model, but no hydrogen atoms were added to noncoordinating ammonia molecules. The crystals of **4** gained so far were very small and of poor quality. Therefore the crystal-structure refinement

Table 1. Crystallographic data for the salts of the anions $[Cu(\eta^4\text{-}Ge_9)(PCy_3)]^{3-}$ (**1a**), $[Cu(\eta^4\text{-}Ge_9)(P\mathit{i}Pr_3)]^{3-}$ (**2a**), and $[Cu(\eta^4\text{-}Ge_9)(\eta^1\text{-}Ge_9)]^{7-}$ (**3a**).

	1	**2**	**3**
Empirical formula	$C_{61.5}H_{128.5}CuGe_9K_3N_{8.5}O_{14.5}P$	$C_{63}H_{168}CuGe_9K_3N_{19}O_{18}P$	$C_{36}H_{135}CuGe_{18}K_7N_{27}O_{12}$
Formula weight	2084.35	2345.28	2782.50
T [K]	150(2)	120(2)	120(2)
Crystal system	trigonal	monoclinic	triclinic
Space group	$P\bar{3}$	$C2/c$	$P\bar{1}$
a [Å]	33.5215(4)	24.7708(7)	14.5267(8)
b [Å]	33.5215(4)	18.3780(5)	17.175(1)
c [Å]	14.4673(3)	47.251(2)	20.869(1)
α [°]	90	90	89.73(1)
β [°]	90	101.88(1)	88.79(1)
γ [°]	120	90	87.97(1)
V [Å^3]	14078.8(4)	21049.7(11)	5202.4(5)
Z	6	8	2
$D_{calcd.}$ [g cm^{-3}]	1.475	1.480	1.771
Absorption coefficient [mm^{-1}]	3.264	2.924	5.643
$F(000)$	6372	9696	2730
Crystal size [mm]	$0.3 \times 0.2 \times 0.2$	$0.4 \times 0.3 \times 0.3$	$0.30 \times 0.15 \times 0.15$
θ range for data collection [°]	2.81 to 25.03	2.75 to 24.71	2.97 to 26.73
Index ranges	$-39 \le h \le 19$	$-29 \le h \le 28$	$18 \le h \le 18$
	$0 \le k \le 39$	$0 \le k \le 21$	$-21 \le k \le 21$
	$0 \le l \le 17$	$0 \le l \le 55$	$0 \le l \le 26$
Reflections collected	283883	176134	89672
Independent reflections (R_{int})	16563 (0.103)	17919 (0.095)	21666 (0.051)
Completeness [%]	99.8	99.8	98.0
Max. and min. transmission	0.659 and 0.391	0.5002 and 0.3161	1.00000 and 0.60094
Data/restraints/parameters	16563/75/527	17919/0/1038	21666/0/925
Goodness-of-fit on F^2	1.085	0.958	1.054
R_1 [$I > 2\sigma(I)$]	0.074	0.055	0.051
wR_2 [$I > 2\sigma(I)$]	0.194	0.138	0.149
R_1 (all data)	0.142	0.095	0.090
wR_2 (all data)	0.208	0.148	0.157
Largest diff. peak and hole [e Å^{-3}]	1.139 and –0.641	1.998 and –0.761	1.426 and –0.904

could not be successfully finished [unit-cell parameter: triclinic, $P\bar{1}$, $a = 10.6864(7)$ Å, $b = 19.587(1)$ Å, $c = 24.841(2)$ Å, $\alpha = 81.81(1)°$, $\beta = 82.10(1)°$, $\gamma = 88.71(1)°$, $V = 5108.25$ Å^3]. Cu and Ge atoms that described a structure of anion **3a** could, however, clearly be located from the measurements. The parameters of data collection, structure solution, and refinement of the parameters for compounds **1**, **2**, and **3** are given in Table 1.

Structure Determination of 1: Throughout all tested crystals, the three cyclohexyl rings and two dmf molecules were found to be strongly disordered. The disorder causes relatively poor data quality, and all carbon, oxygen, and nitrogen atoms were refined with isotropic displacement parameters. The cyclohexyl rings and one dmf molecule were refined with split positions. All C–C bond lengths in the cyclohexyl rings were fixed to 1.45(3) Å. The disordered solvent molecules were adapted to a structure model using the parameters of another well-ordered molecule (SAME routine). Large voids in the crystal structure hint towards further unlocated solvent molecules, and the remaining electron density was treated with the PLATON SQUEEZE routine.[42,43] The asymmetric unit clasps three solvent molecules, one of which was disordered around the center of inversion in the Wyckoff position *3f* and was thus refined with a site-occupation factor of 0.5.

Structure Determination of 2: One disordered ammonia molecule was refined isotropically with split positions. The N atom of one solvent molecule was situated on the Wyckoff position *4e*, whereas a second lay close to it and was refined with a site-occupation factor of 0.5.

CCDC-751495 (for **1**), -751496 (for **2**), and -751497 (for **3**) contain 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.

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