Homoatomic Polyhedra as Structural Modules in Chemistry: What Binds Fullerenes and Homonuclear Zintl Ions?**

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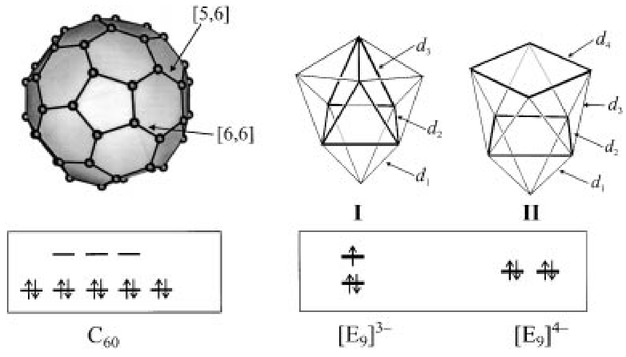
Ligand-free homoatomic polyhedra are fascinating, not only because of their aesthetic simplicity but also because of their physical and chemical properties. They serve as electron reservoirs, show structural changes that depend upon the electron count, and can be used as "super-atomic" building blocks for the targeted assembly of complex structures. Herein, the increasingly pronounced relationship between the fullerides and the nine-atom Zintl ions, the terels, is considered, even though one class of the compounds can be described as large polyhedra with classical bonds and the other as small clusters with nonclassical bonds (Wade rules). In both classes soluble salts with isolated ions, polymer chains, and binary phases with strong interactions between the ions occur.



Scheme 1. The structures and degenerate valence orbitals of a) fullerene C_{60} and b) the Zintl ions $[E_9]^{3-}$ and $[E_9]^{4-}$.

The beauty[1] of nine-atom polyhedra E_9 of heavy elements from the carbon subgroup does not pale to the aesthetics of carbon fullerenes. Zintl ions of Group 14 elements and fullerenes are remarkable because they form highly symmetrical homoatomic polyhedral frameworks of varying size (Scheme 1). Polyhedral E_9 clusters have been the subject of intensive investigation for several decades,[2–6] long before the fullerenes were discovered.[7] Along with the boom in fullerene chemistry,[8] which started with the large-scale synthesis of C_{60},[9] recent years have also marked a growing renaissance in the chemistry of homoatomic Zintl ions.[10–13] The parallels between the two fields,[13] rather unnoticed before, have been impressively confirmed with the synthesis of anionic polymeric chains containing connected ${}^{1}_{\infty}\{C_{70}{}^{2-}\}$[14] and ${}^{1}_{\infty}\{[Ge_9]^{2-}\}$ ions[15] (Figure 1 a and b).

Since the discovery of C_{60}, a large number of C_n molecules and C_n anions have been reported; however, only a few were structurally characterized in the solid state. Most of the research was focused on the C_{60} and C_{70} molecules, which are relatively easy to obtain compared to other fullerenes.[16–18] In contrast, a large number of structures have been characterized for E_n polyhedra containing the heavy homologues of carbon (E = Si, Ge, Sn, Pb). Many structures of anions such as $[E_4]^{4-}$, $[E_4]^{6-}$, $[E_5]^{2-}$, $[E_6]^{2-}$, $[E_9]^{3-}$, $[E_9]^{4-}$, and $[E_{10}]^{2-}$ are known from single-crystal X-ray structure analysis. There are also mass spectrometry data for the heavy homologues, confirming the existence of larger cluster anions $[E_n]^-$ and $[AE_n]^-$[19] and cations $[A_mE_n]^+$ (A = alkali metal).[20]

Besides the preferred formation of homoatomic polyhedra, the reactivity of fullerenes and fullerene anions also displays remarkable analogy to the chemistry of homoatomic Zintl ions. This parallel is, however, not all that surprising if homoatomic Zintl ions of Group 14 elements are regarded as heavy homologues of the fullerenes. In the fullerene family, the C_{60} and C_{70} molecules are outstanding due to their stability and developed synthetic routes. For homoatomic clusters, E_4 and E_9 frameworks are the most frequent for E = Si to Pb. Anionic E_9 clusters with E = Ge, Sn, and Pb are also stable in solution and thus, like fullerenes and fullerides, can be used for reactions in solution. A controlled arrangement of redox-active polyhedral C_n and E_n units over one, two, or three dimensions opens a new way to the "bottom-up" synthesis of materials with switchable electronic properties. Covalent bonding between polyhedra leads to stable aggregates. In comparison with supramolecular structures based on C_{60} with relatively weak interactions between the units,[21, 22] these covalent aggregates could be retained even upon reduction or

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[**] This work was supported by the Deutsche Forschungsgemeinschaft.

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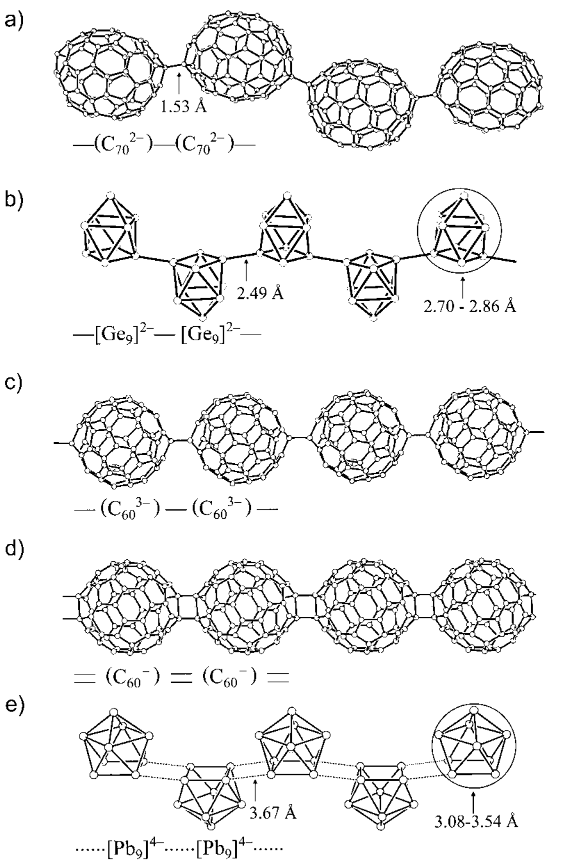

Figure 1. Structural fragments of linear polymers: a) $^{1}_{\infty}\{C_{70}^{2-}\}$ in $[Ba(NH_3)_9][C_{70}](NH_3)_7$,[14] b) $^{1}_{\infty}\{[Ge_9]^{2-}\}$ in $[K([18]crown\text{-}6)]_2[Ge_9](en)$ (en = ethylenediamine),[15] c) $^{1}_{\infty}\{C_{60}^{3-}\}$ in Na_2RbC_{60},[36] d) $^{1}_{\infty}\{C_{60}^{-}\}$ in RbC_{60},[38] e) the arrangement of $[Pb_9]^{4-}$ ions in K_4Pb_9.[49]

oxidation and, with the proper choice of covalent bridge, could exhibit an electronic interaction between the units.

In the following the close relationship of the C_{60} and C_{70} fullerenes to nine-atom clusters of heavy tetrel elements is discussed on the basis of structural aspects, mostly taking into account the compounds that are unambiguously structurally characterized. All the structures of the E_9 clusters in question are ordered and were determined using X-ray diffraction methods on single crystals. In the case of fullerenes and fullerides, due to the lack of single-crystal data, controversial structural models are also included. Parallels between electronic and magnetic properties are pointed out, when appropriate.

Fullerene carbon cages represent frameworks of strong covalent bonds, which can be described in terms of two-center, two-electron bonds and a conjugated π system. The localization of double bonds leads to different interatomic distances for the [6,6] and [5,6] ring connections (1.38 and 1.45 Å, respectively, Scheme 1). When the fullerenes are reduced to the sixfold negatively charged ions C_{60}^{6-}[23] (Scheme 1, left) and C_{70}^{6-}, their frameworks are preserved.[24] Jahn–Teller distortions, which are expected on the way from neutral cages to the maximally reduced anions in the case of nonsymmetrical population of the degenerate LUMOs of C_{60}, are structurally hardly noticeable.[17, 25, 26] In this respect nine-atom Zintl ions behave very differently. Their frameworks possess structures inbetween the trigonal tricapped prism **I** and the monocapped square antiprism **II** (Scheme 1, right). Structure **I** features three different interatomic distances ($d_2 > d_3 > d_1$), while structure **II** has two ($d_2 > d_1 \approx d_3 \approx d_4$).[27] The expected structure type can be rationalized using the electron counting rules developed by Wade for boranes and carboranes, provided that the B–H and C–H *exo* bonds of homoatomic clusters are substituted by free electron pairs. According to Wade's rules, anions $[E_9]^{2-}$ and $[E_9]^{4-}$ with 38 and 40 valence electrons should possess structures of the *closo* type **I** and *nido* type **II**, respectively. Oxidation of the *nido*-cluster should lead to a distinct change of the structure. Until now, only 39- and 40-electron clusters are unequivocally characterized. In solution and at room temperature the different atomic positions of the $[Sn_9]^{4-}$ and $[Pb_9]^{4-}$ ions are indistinguishable on the NMR timescale. The flexibility of the polyhedra reveals itself in the solid state. A large number of structural investigations of salts containing large counterions (and therefore clusters with only van der Waals type interactions) and binary Zintl phases with strong interactions between the ions have demonstrated that the $[E_9]^{4-}$ polyhedra can undergo strong distortions independant of crystal packing.[13] Many clusters do not strictly obey Wades' rules.

Fullerenes and Zintl ions both form stable radicals. The ESR signals were registered for C_{60}^{x-} ($x = 1-5$) and C_{70}^{-}. The interpretation of the spectra is complex since the energy differences between the possible spin states are small, the effects of disproportionation and dimerization must be taken into account in solution, and samples that are available only in the solid state are often poorly characterized. Magnetic measurements are more reliable; however, up to now they also failed to provide a fully coherent picture.[17, 26] Paramagnetic species $[E_9]^{3-}$ are readily available by oxidation of $[E_9]^{4-}$. The ESR spectra of single crystals and powder suggest the existence of radicals for E = Ge, Sn, and Pb. Magnetic measurements for E = Sn and Pb also indicate that compounds with mixed-valent anions $[E_9]^{2-}/[E_9]^{4-}$ are formed.[28] Distortions of the polyhedra, observed for $[E_9]^{3-}$ ions, may be regarded as a pronounced Jahn–Teller effect (Scheme 1).

In spite of substantial differences in chemical bonding and framework flexibility, fullerides and E_9 clusters equally function as ligands in transition metal complexes. Unsubstituted C_{60} acts as a η^2 ligand (Figure 2a), which is in agreement with limited aromaticity[29] and alternating double and single bonds of [6,6] and [5,6] ring connections. Metal atoms are coordinated by the [6,6] double bond. Substituted fullerenes display η^5 coordination, as the example of $[(\eta^5\text{-}Ph_5C_{60})Tl]$ shows.[30] For E_9 clusters η^4 coordination to the $Cr(CO)_3$ fragment is exclusively observed (Figure 2b; E = Sn, Pb). In salts with $[A^+([18]crown\text{-}6)]$ counterions, C_{60}^{3-} and $[E_9]^{4-}$ ions coordinate the alkali metal atoms.[31] In $[K([18]crown\text{-}6)]_3[\eta^6,\eta^6\text{-}C_{60}](\eta^3\text{-}C_6H_5CH_3)_2$ two potassium cations sit unsymmetrically above the six-membered rings of the fullerene trianions (Figure 2c), while E_9 polyhedra prefer to coordinate with their triangular faces.[32] However, coordination involving square faces of the polyhedron is also possible (Figure 2d).[33] Finally, there are two-dimensional layers of C_{60}^{2-} ions and one-dimensional arrangements of E_9 clusters in the

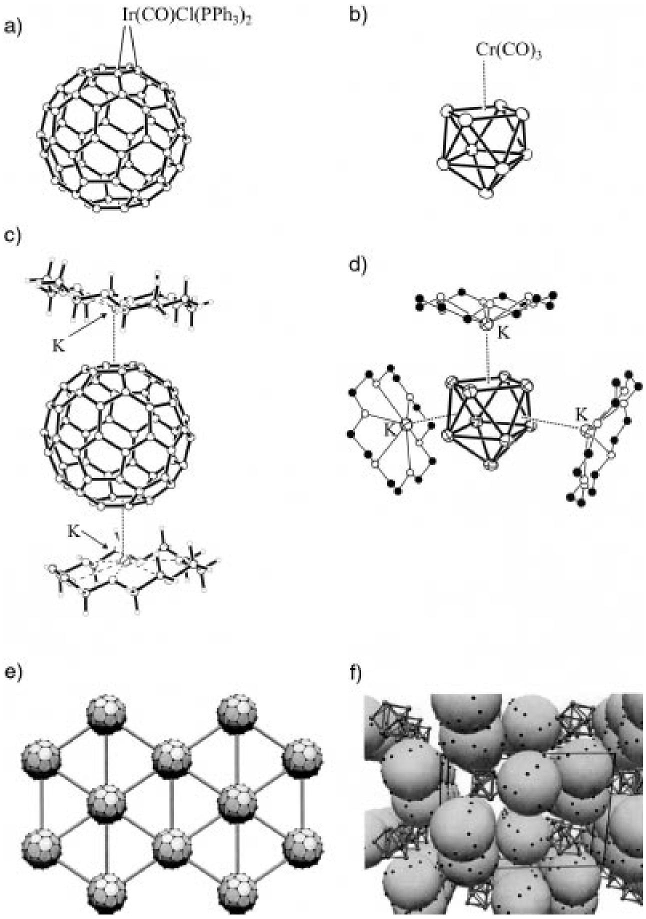

Figure 2. The structures and structural fragments of complexes: a) $[(\eta^2\text{-}C_{60})Ir(CO)Cl(PPh_3)_2]$,[50] b) $[K([2.2.2]crypt)]_4[(CO)_3Cr][\eta^4\text{-}E_9]$ (E = Sn, Pb),[51, 52] c) $[K([18]crown\text{-}6)]_3[\eta^6,\eta^6\text{-}C_{60}](\eta^3\text{-}C_6H_5CH_3)_2$,[26] d) $[K([18]crown\text{-}6)]_4[\eta^3,\eta^3,\eta^4\text{-}Pb_9]$,[33] e) the layer of C_{60}^{2-} ions in $[K([2.2.2]crypt)]_2[C_{60}](C_6H_5CH_3)_4$,[53] f) the arrangement of $[Ge_9]^{3-}$ clusters in $[K([2.2.2]crypt)]_3[Ge_9](en)_{0.5}$[54] (the [K([2.2.2]crypt)] units are shown as large spheres, the carbon atoms as black dots).

salts with $[K^+([2.2.2]crypt)]$ counterions.[34] The distances between the centers of mass of the polyhedra are longer than 12.8 and 8 Å for the examples shown in Figures 2e and 2f, respectively.

Fullerides and E_9 clusters both form binary and ternary phases with alkali metals. Phases of the composition A_3C_{60} and $A_{3-x}A'_xC_{60}$ have been studied with particular intensity[35] due to their superconducting properties. The $Na_2A'C_{60}$ (A′ = K, Rb, Cs)[36, 37] and AC_{60} (A = K, Rb, Cs)[38] phases feature short distances between the C_{60} anions. Although the carbon positions cannot be unambiguously determined from the X-ray powder data, the polymers shown in Figure 1c and 1d are obtained as the best fit of the data using the Rietveld method. The two polymer structures show only small differences in the distances between the centers of the polyhedra (9.36 Å in Na_2RbC_{60}[37] and 9.14 Å in RbC_{60}[38]). The bonds between the anions result from the different orientations of the fullerene molecules. The fit was performed by gradual rotation of the C_{60} molecule and produced only small differences in the *R* factors for both models. In Na_2RbC_{60} the C_{60}^{3-} ions are connected by a C–C single bond. Its length after multiple successive refinement steps was determined to be 1.70 Å. In AC_{60} the bonding between the C_{60}^{-} ions is analogous to a [2+2] cycloaddition of two bonds. The C_{60}^{-} ions are connected through [6,6] bonds, which are elongated to the outstanding value of 1.90 Å (Figure 1d), forming the four-membered cycle. The shortest distance between carbon atoms of two neighboring fullerenes is 1.43 Å and thus within the range of a C–C single bond. The phase diagram of alkali metals and C_{60} are complex, and often the quality of the X-ray powder data is insufficient. Therefore, the models shown in Figure 1c and 1d are rather questionable and still the subject of discussion.[39] Noteworthy is a similar linear arrangement of the $[Pb_9]^{4-}$ ions in K_4Pb_9.[40] There are also two relatively short distances between polyanions (Figure 1e).[41] The *exo* bonds are only slightly longer than the interatomic distances in polyhedra and, hence, longer than typical Pb–Pb single bonds. Polymerization of Zintl ions in the solid state is known and was first studied on the example of Ba_3Ge_4 single crystals. Isolated $[Ge_4]^{6-}$ clusters with a butterfly structure of the high-temperature phase $\beta\text{-}Ba_3Ge_4$ Link into chains $^1_\infty\{[Ge_4]^{6-}\}$ in the α phase at lower temperature.[42]

Successful aggregation of anions in solution into one-dimensional polymers opens new possibilities for the design and construction of nanostructures. This point is proven by the examples of single-crystal analysis from fullerene chemistry and Zintl ion chemistry. By the route known since 1891—namely, reduction of the elements in liquid ammonia[2]—the linear polymer $(C_{70}^{2-})_n$ (Figure 1a) was synthesized from C_{70} and Ba. Extraction of a solidified K/Ge melt with ethylenediamine and subsequent addition of [18]crown-6 provides the polymer $([Ge_9]^{2-})_n$ (Figure 1b). While in the carbon polymers the C–C distances between fullerenes are longer than the intramolecular C–C distances, the polymer containing E_9 clusters features *exo* bonds that are shorter than the intramolecular bonds (see also Figure 3c). The reason for this is the presence of longer, delocalized bonds within the cluster polyhedra, compared to element–element single bonds.

The formation of dimers may be seen as the first step in the synthesis of a polymer. There are only a few such examples among the fullerenes and Zintl ions, nevertheless the parallels are also evident. Tribochemical treatment of the C_{60} with KCN leads to the formation of the dumbbell-shaped dimer $C_{60}\text{–}C_{60}$, in which two C_{60} molecules are bonded through [6,6] ring elements analogous to a [2+2] addition.[43] This is the only example of a compound with linked C_{60} molecules whose structure has been reliably determined from single-crystal data. In contrast to the polymer in Figure 1d, the bonds in the four-membered ring connecting the molecules are almost equal (1.58 and 1.57 Å). On rapid cooling of the alkali metal fullerides of the composition AC_{60} to room temperature, a metastable phase can be obtained that, analogous to the chain shown in Figure 1c, contains $(C_{60}\text{–}C_{60})^{2-}$ dimers that are connected by a C–C single bond. The tilting of the $(C_{60}\text{–}C_{60})$ units in the polymeric chain would lead to the suggested dimers. The distortion of the chain is only indicated by the appearance of weak superstructure reflections in the X-ray powder pattern.[44] The heavy-element counterpart is the dimer of two connected Ge_9 clusters $([Ge_9]\text{–}[Ge_9])^{6-}$.[45] The X-ray single-crystal investigation of the polymer provided the bonding parameters shown in Figure 1b and proved that the clusters are connected by a Ge–Ge single bond.

Quite surprising is the fact that for the two examples shown in Figure 3a and c there are structures with similar orientations of two C_{60}^{3-} or two $[Sn_9]^{4-}$ ions, but with longer intermolecular distances. In $[K([18]crown\text{-}6)]_3[\eta^6,\eta^6\text{-}C_{60}](\eta^3\text{-}C_6H_5CH_3)_2$ the shortest distances between the carbon atoms of two C_{60}^{3-} ions turn out to be between the [5,6] ring bonds (Figure 3b).[26] Analogous to the germanium dimer, in $[K([18]crown\text{-}6)]Cs_7[Sn_9]_2$ there are two $[Sn_9]^{4-}$ clusters with almost the same orientation with respect to each other and similar coordination of bridging Cs cations (Figure 3d). The distance between the clusters is, naturally, significantly longer than the distances between the atoms within the cluster.[46]

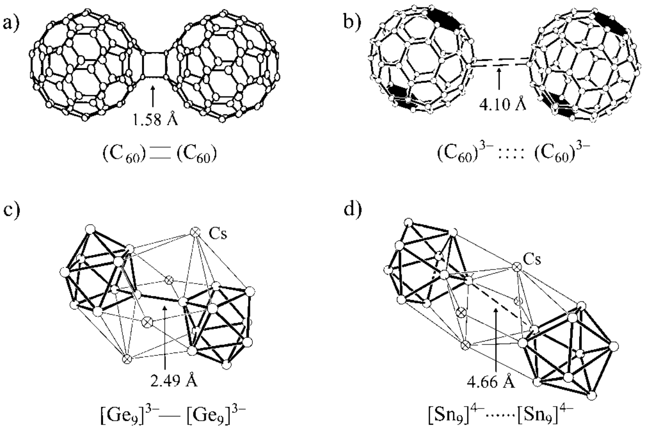

Figure 3. The structures and structural fragments of dimeric polyhedral units: a) $(C_{60})_2$,[43] b) C_{60}^{3-} ion pairs in $[K([18]crown\text{-}6)]_3[\eta^6,\eta^6\text{-}C_{60}](\eta^3\text{-}C_6H_5CH_3)_2$[26] (black shading shows the fragments coordinating potassium atoms, see Figure 2c), c) dimeric unit in $[K([2.2.2]crypt)]_2Cs_4([Ge_9]{-}[Ge_9])$[45], d) $[Sn_9]^{4-}$ ion pairs in $[K([18]crown\text{-}6)]Cs_7[Sn_9]_2(en)_4$.[46]

In summary, we can state that in solution fullerenes and fullerides have been better characterized than Zintl ions. Also, in the solid state fullerene compounds feature more interesting properties, such as superconductivity in A_3C_{60}. Since many of the fulleride structures are not unequivocally known, structure–property relationships can only be established in a few cases. In contrast, while the structures of many Zintl ions have been reliably determined, little is known about the physical properties of compounds containing such ions. Successful structural characterization of the ${}^{1}_{\infty}\{C_{70}^{2-}\}$ and ${}^{1}_{\infty}\{[Ge_9]^{2-}\}$ polymers from single-crystal data probably presents a milestone on the way to the controlled arrangement of clusters that may serve as electron reservoirs. We will be waiting with great interest to discover which compound turns out to possess more intriguing properties.

What is to follow? Polymers with mixed structural modules are quite possible, probably upon inclusion of particular bridging atoms between different types of polyhedra. Controlled design of large oligomers and multidimensional polymers? In the field of fullerene chemistry two- and three-dimensional linked systems are being discussed. Carbon-based polymers built from the polyhedral modules are obtained by photochemical reactions or by high-pressure and high-temperature treatment of C_{60} and C_{70}. Indeed, many structures that have been determined for this class of compounds are based on the comparison between various structural models and not on the independent structure refinement.[47] Figure 4a shows the structure of the ${}^{2}_{\infty}[C_{60}]$ polymer resulting from [2+2] cycloaddition. Rietveld analysis indicates that Na_4C_{60} contains a two-dimensional arrangement of C_{60}^{4-} ions, connected by four single bonds (Figure 4b).[48] Two-dimensional polymers consisting of E_9 monomers are yet to be discovered; however, a (supramolecular?) layer framework of Cs^+ and Sn_9^{4-} ions was found between the weakly bonded layers of $[K^+([18]crown\text{-}6)]$ units.[46] Analogous to the formation of the dimer $([Ge_9]{-}[Ge_9])^{6-}$ and the one-dimensional polymer ${}^{1}_{\infty}\{[Ge_9]^{2-}\}$ upon oxidative coupling [Eq. (1) and (2)], the next oxidative step would probably lead to the two-dimensional polymer ${}^{2}_{\infty}\{[Ge_9]\}$ [Eq. (3)]. The result would be a neutral, crystalline germanium allotrope built from Ge_9 modules (Figure 4c). It is worth the challenge!

$$2\ [Ge_9]^{4-} \longrightarrow ([Ge_9]{-}[Ge_9])^{6-} + 2\,e^- \qquad (1)$$

$$n/2\ ([Ge_9]{-}[Ge_9])^{6-} \longrightarrow (-[Ge_9]^{2-}-)_n + n\,e^- \qquad (2)$$

$$(-[Ge_9]^{2-}-)_n \longrightarrow (-\underset{|}{\overset{|}{[Ge_9]}}-)_n + 2n\,e^- \qquad (3)$$

Received: May 28, 2001 [M1515]

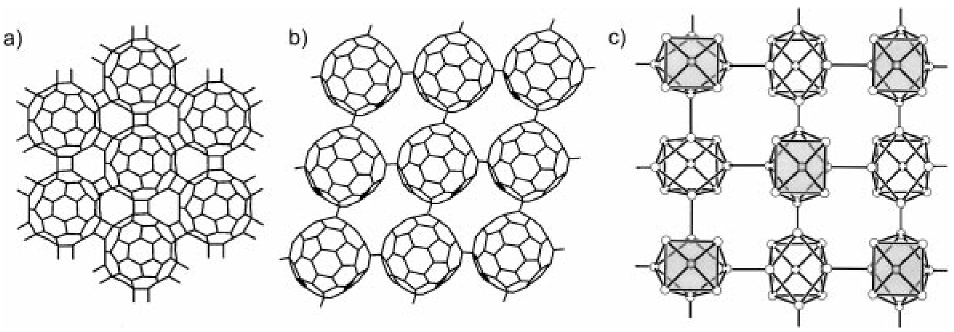

Figure 4. The structural models of a) the polymer ${}^{2}_{\infty}\{C_{60}\}$[47] obtained by high-pressure and high-temperature synthesis and b) the two-dimensional polymer ${}^{2}_{\infty}\{C_{60}^{4-}\}$ in Na_4C_{60}.[48] c) The suggested structure of a germanium allotrope in the form of the two-dimensional polymer ${}^{2}_{\infty}\{[Ge_9]\}$; the type **II** clusters are drawn with their square face alternating up and down.

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