(Quantum Design) in the temperature range 5 to 300 K. The output data were corrected for the diamagnetism of the sample holder and of the samples, calculated from their Pascal's constants.

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[1] D. M. J. Doble, C. H. Benison, A. J. Blake, D. Fenske, M. S. Jackson, R. D. Kay, W.-S. Li, M. Schröder, *Angew. Chem.* **1999**, *111*, 2042; *Angew. Chem. Int. Ed.* **1999**, *38*, 1915.

[2] J. Lisowski, P. Starynowicz, *Inorg. Chem.* **1999**, *38*, 1351.

[3] A. J. Blake, R. O. Gould, C. M. Grant, P. E. Y. Milne, S. Parsons, R. E. P. Winpenny, *J. Chem. Soc. Dalton Trans.* **1997**, 485; E. K. Brechin, S. G. Harris, S. Parsons, R. E. P. Winpenny, *J. Chem. Soc. Dalton Trans.* **1997**, 1665.

[4] J.-P. Costes, F. Dahan, A. Dupuis, J.-P. Laurent, *Inorg. Chem.* **1997**, *36*, 3429.

[5] X.-M. Chen, S. M. J. Aubin, Y.-L. Wu, Y.-S. Yang, T. C. W. Mak, D. N. Hendrickson, *J. Am. Chem. Soc.* **1995**, *117*, 9600; X.-M. Chen, Y.-L. Wu, Y.-Y. Yang, S. M. J. Aubin, D. N. Hendrickson, *Inorg. Chem.* **1998**, *37*, 6186.

[6] A. Bencini, C. Benelli, A. Caneschi, R. L. Carlin, A. Dei, D. Gatteschi, *J. Am. Chem. Soc.* **1985**, *107*, 8128.

[7] M. Andruh, I. Ramade, E. Codjovi, O. Guillou, O. Kahn, J. C. Trombe, *J. Am. Chem. Soc.* **1993**, *115*, 1822.

[8] I. Ramade, O. Kahn, Y. Jeannin, F. Robert, *Inorg. Chem.* **1997**, *36*, 930.

[9] C. Benelli, A. Caneschi, D. Gatteschi, O. Guillou, L. Pardi, *Inorg. Chem.* **1990**, *29*, 1750.

[10] J. L. Sanz, R. Ruiz, A. Gleizes, F. Lloret, J. Faus, M. Julve, J. J. Borrás-Almenar, Y. Journaux, *Inorg. Chem.* **1996**, *35*, 7384.

[11] Y. Yukawa, S. Igarashi, A. Yamano, S. Sato, *Chem. Commun.* **1997**, 711.

[12] Y. Cui, J.-T. Chen, D.-L. Long, F.-K. Zheng, W.-D. Cheng, J.-S. Huang, *J. Chem. Soc. Dalton Trans.* **1998**, 2955.

[13] N. Sakagami, K. Okamoto, *Chem. Lett.* **1998**, 201.

[14] D. M. L. Goodgame, S. Menzer, A. T. Ross, D. J. Williams, *J. Chem. Soc. Chem. Commun.* **1994**, 2605.

[15] J. Liu, E. A. Meyers, J. A. Cowan, S. G. Shore, *Chem. Commun.* **1998**, 2043.

[16] S. Decurtins, M. Gross, H. W. Schmalle, S. Ferlay, *Inorg. Chem.* **1998**, *37*, 2443.

[17] T.-Z. Jin, S.-F. Zhao, G.-X. Xu, Y.-Z. Han, N.-C. Shi, J.-S. Ma, *Acta Chim. Sinica* **1991**, *49*, 569.

[18] J.-G. Mao, L. Song, J.-S. Huang, *J. Chem. Cryst.* **1998**, *28*, 475.

[19] A. Rabenau, *Angew. Chem.* **1985**, *97*, 1017; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 1026; R. A. Ludise, *Chem. Eng. News* **1987**, *65*(40), 30; J. Y. Lu, M. L. Lawandy, J. Li, T. Yuen, C. L. Lin, *Inorg. Chem.* **1999**, *38*, 2695, and references therein.

[20] Crystal data for **1**: Crystal dimensions $0.12 \times 0.12 \times 0.08$ mm, $C_{42}H_{50}N_6O_{40}Cu_3Gd_2$, $M_w = 1784.0$, triclinic, space group $P\bar{1}$, $a = 7.393(2)$, $b = 13.576(6)$, $c = 15.169(4)$ Å, $\alpha = 72.62(2)$, $\beta = 76.15(2)$, $\gamma = 80.17(3)^\circ$, $V = 1401.7(7)$ Å^3, $Z = 1$, $R(wR) = 0.043(0.097)$ for 4906 reflections with $F \geq 2.0\sigma(F_o)$. Crystal data for **2**: Crystal dimensions $0.45 \times 0.20 \times 0.15$ mm, $C_{56}H_{56}N_8O_{48}Cu_2Gd_4$, $M_w = 2365.2$, monoclinic, space group $P2_1/c$, $a = 9.260(2)$, $b = 25.543(5)$, $c = 7.782(1)$ Å, $\beta = 97.36(2)^\circ$, $V = 1825.3(6)$ Å^3, $Z = 1$, $R(wR) = 0.034(0.088)$ for 3179 reflections with $F \geq 2.0\sigma(F_o)$. The intensity data were collected on a Bruker CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation at room temperature. The structures were solved by directed methods and all of the calculations were performed by using the SHELXTL-93 program package on a Legand computer. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-138940 for **1** and -138941 for **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Experimental Observation of Pentaatomic Tetracoordinate Planar Si- and Ge-Containing Molecules: MAl$_4^-$ and MAl$_4$**

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The chemistry of silicon and germanium is dominated by their tendency to form tetracoordinate tetrahedral structures, just as their more famous congener, the tetracoordinate tetrahedral carbon atom. The tetrahedral carbon idea, proposed by van't Hoff and Le Bel 125 years ago, has been the most important stereochemistry concept in understanding organic and biomolecules. The tetracoordinate tetrahedral structure of C, Si, and Ge atoms is rationalized elegantly by the concept of sp^3 hybridization. However, in the last 30 years chemists have attempted to make unusual compounds that contain *planar* tetracoordinate C, Si, and Ge atoms. In particular, substantial efforts and progress have been made in the design and synthesis of tetracoordinate planar carbon molecules by overcoming the inherent preference for tetrahedral bonding.[1–6] Tetracoordinate planar silicon molecules have also been studied theoretically[7] and experimentally.[8]

We are interested in the genertion of planar carbon, silicon, germanium, tin, and lead species in the gas phase and the investigation of their electronic structure and chemical bonding by using a combined experimental and theoretical approach. We recently reported the first observation of a *pentaatomic* tetracoordinate planar carbon molecule (CAl$_4^-$) which has a planar structure and represents the smallest species to contain a tetracoordinate planar carbon.[9] Interestingly, however, its neutral CAl$_4$ parent molecule is tetrahedral. We showed that planarity in CAl$_4^-$ is achieved through ligand–ligand bonding interactions in its HOMO. We also found a general rule, that to achieve planarity in pentaatomic species composed of a first-row central atom and second- or

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third-row ligand atoms, these species should possess 17 or 18 valence electrons.[9–11]

It is, however, not clear if the planar structure will be preserved when the first-row central atom is substituted by a second- or third-row atom. These molecules would be isoelectronic with the species that contain a first-row central atom, but the central cavity may be too small to accommodate the second- or third-row atom in the planar square structure. Herein we address this question by investigating $SiAl_4^-$ and $GeAl_4^-$ and their corresponding neutral molecules.

The experiments were performed with a magnetic-bottle time-of-flight photoelectron spectroscopy apparatus with a laser vaporization cluster source.[12, 13] The $SiAl_4^-$ and $GeAl_4^-$ ions were produced by laser vaporization of the corresponding mixed targets (Si/Al and Ge/Al) with pure helium carrier gas. The 532 and 355 nm spectra of $SiAl_4^-$ and $GeAl_4^-$ are shown in Figure 1. The 532 nm spectrum of $SiAl_4^-$ (Figure 1 a) revealed a partially vibrationally resolved band with an average spacing of 220 cm^{-1}. The adiabatic electron detachment energy (ADE) of $SiAl_4^-$ was determined from the 0-0 transition to be 2.094 eV and its vertical electron detachment energy (VDE) was measured to be 2.121 eV. At 355 nm (Figure 1c), several more features were observed. The feature at 2.7 eV (labeled A) shows a splitting which does not seem to be a vibrational progression. According to our theoretical result (see below), this splitting corresponds to a possible triplet–singlet splitting caused by detachment of a $3b_2$ electron. A broad feature (B) was observed around 2.9 eV, followed by a feature (C) at 3.16 eV. The spectra of $GeAl_4^-$ are nearly identical to those of $SiAl_4^-$, which indicates that the anions were correctly selected, as these two isoelectronic species are expected to have similar electronic and molecular structures. The 532 nm spectrum (Figure 1 b) of $GeAl_4^-$ also revealed a partially vibrationally resolved band with a smaller vibrational spacing of 160 cm^{-1}. The ADE of $GeAl_4^-$ is identical to that of $SiAl_4^-$ within our experimental accuracy. The VDE of $GeAl_4^-$ was measured to be 2.114 eV. At 355 nm (Figure 1 d), again several more features (A--C) were observed, similar to those of $SiAl_4^-$. All the observed ADEs and VDEs for $SiAl_4^-$ and $GeAl_4^-$ are given in Table 1.

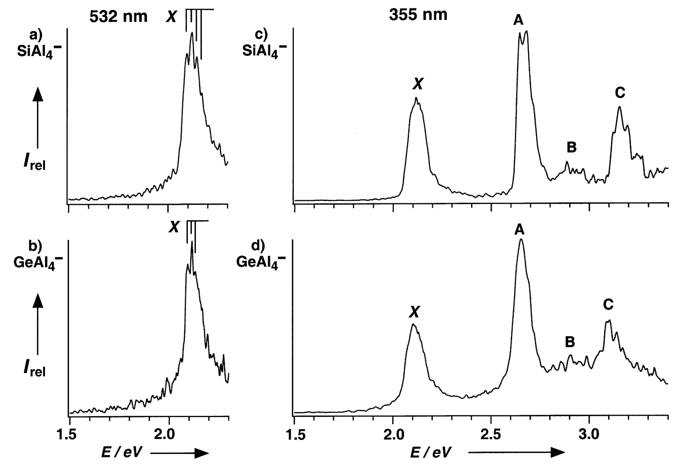

Figure 1. Photoelectron spectra of $SiAl_4^-$ and $GeAl_4^-$ at 532 nm (2.331 eV) and 355 nm (3.496 eV), plotted in increasing electron binding energy. The four observed detachment channels are labeled (*X*, A, B, and C). The vertical lines in (a) and (b) indicate vibrational structures.

Table 1. Experimental and theoretical VDE and ADE of $SiAl_4^-$ and $GeAl_4^-$.

State	Experimental ADE [eV]	Experimental VDE [eV]	Detachment channel[a]	Theoretical VDE [eV][b]	Theoretical ADE [eV][b]
$SiAl_4^-$					
X	2.121 (0.020)	2.094 (0.020)	$5a_1$ ($^1A_1$)	2.00	2.00
A	2.65 (0.03)	2.65 (0.03)	$3b_2$ ($^3B_2$)	2.57	
B	≈2.9	≈2.8	$4a_1$ ($^3A_1$)	3.01	
C	3.16 (0.03)	3.11 (0.03)	$1b_1$ ($^3B_1$)	3.47	
$GeAl_4^-$					
X	2.114 (0.020)	2.094 (0.020)	$5a_1$ ($^1A_1$)	2.03	2.02
A	2.66 (0.06)	2.66 (0.06)	$3b_2$ ($^3B_2$)	2.56	
B	≈2.9	≈2.8	$4a_1$ ($^3A_1$)	3.00	
C	3.10 (0.03)	3.08 (0.04)	$1b_1$ ($^3B_1$)	3.35	

[a] $4a_1$ is the ligand–ligand bonding MO; the other three orbitals are ligand-centered nonbonding lone-pair MOs (see Figure 3). The final state is given in parentheses. [b] The $5a_1$ MO is singly occupied in the anions. Thus, the first detachment channel corresponds to a singlet final state (ground state of the neutral) and all the other detachment channels correspond to triplet final states. All data are at the CCSD(T)/6-311+G(2df)//MP2/6-311+G* level of theory.

In our ab initio calculations,[14, 15] we considered in detail neutral $SiAl_4$ and $GeAl_4$ molecules and their anions. We performed a complete search for the global minimum of $SiAl_4$ and its anion. For $GeAl_4$, we assumed that it would have a similar global minimum to that of $SiAl_4$, based on their nearly identical photoelectron spectra (Figure 1). The lowest energy anion structures for each cluster are shown in Figure 2. Indeed, both $SiAl_4^-$ and $GeAl_4^-$ were found to be planar and contain tetracoordinate Si and Ge atoms (valence electronic configuration: $1a_1^2\ 1b_2^2\ 2a_1^2\ 3a_1^2\ 2b_2^2\ 1b_1^2\ 4a_1^2\ 3b_2^2\ 5a_1^1$). As expected, the small cavity formed by an Al_4 square was too small to accommodate Si or Ge atoms and the molecules are distorted into C_{2v} symmetry. Surprisingly and in contrast to

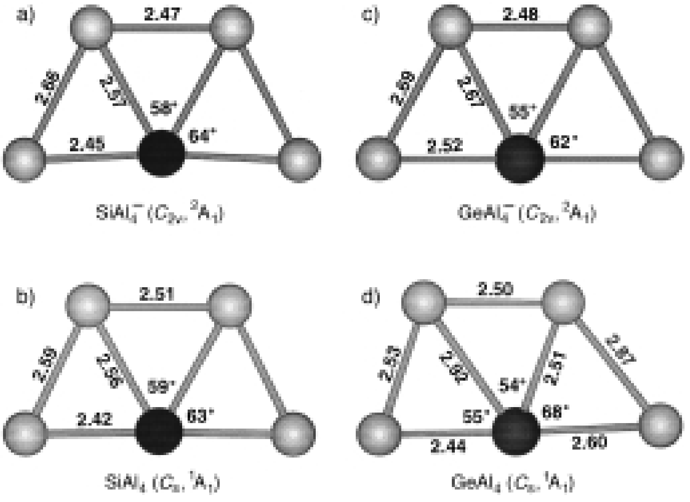

Figure 2. Ab initio structures of $SiAl_4^-$, $SiAl_4$, $GeAl_4^-$, and $GeAl_4$ optimized at the MP2/6-311+G* level of theory and showing the bond lengths [Å] and angles [°]. Note that $SiAl_4$ (b) is not planar, the two Al atoms appearing to be on the same line as Si are actually each 11° above the plane, giving a 158° ∢Al-Si-Al angle, which cannot be seen in the two-dimensional plot.

CAl_4, the neutral $SiAl_4$ and $GeAl_4$ molecules are not tetrahedral.[9] The $GeAl_4$ molecule remains planar, whereas $SiAl_4$ is quasi-planar with the two Al units at the apices each being out of plane by 11° (Figure 2). However, the barrier to planarity for $SiAl_4$ after the zero-point energy (ZPE) corrections was found to be just 0.26 $kcal\,mol^{-1}$ (MP2). We did find T_d local minima for $SiAl_4$ and $GeAl_4$, but they are 27 $kcal\,mol^{-1}$ (MP2) higher in energy than the structures shown in Figure 2.

In Table 1 we present results of our calculations of the four lowest-lying vertical one-electron detachment processes from the tetracoordinate planar global-minimum structures of $SiAl_4^-$ and $GeAl_4^-$ (that is from the $5a_1$, $3b_2$, $4a_1$, and $1b_1$ orbitals, respectively) and compare them with the experimental data. Removal of the single electron from the $5a_1$ orbital results in the $^1A_1$ ground state for the neutral species. The calculated ADE and VDE of this detachment channel agree well with the experimental values (Table 1). Detachment from the $3b_2$, $4a_1$, and $1b_1$ orbitals will each result in both triplet and singlet excited states for the neutral species. Only the triplet final states are considered here, because the final singlet excited states require multiconfigurational references and cannot be treated by the CCSD(T) method used here. The calculated VDEs for the triplet excited states agree well with the major experimental features (A–C). The singlet excited states are likely to be close in energy to the corresponding triplet states. The splitting observed for the feature A in the 355 nm spectrum of $SiAl_4^-$ is probably because of the singlet state. Both the features B and C are relatively broad and may conceivably contain the singlet states as well. The overall excellent agreement between the theoretical and experimental results of the global-minimum tetracoordinate planar structures provide solid evidence that we have indeed identified the first *pentaatomic* tetracoordinate planar silicon and germanium molecules in their anion states.

Our previous work provided the tetracoordinate planar carbon anion in CAl_4^-, whereas the neutral CAl_4 has a tetrahedral structure. Our previous experimental observation of an extremely broad $(X, CAl_4^-) \rightarrow (X, CAl_4)$ transition in the photoelectron spectra of CAl_4^- provided conclusive evidence for the large geometry changes from the planar square structure of CAl_4^- to the tetrahedral structure of CAl_4.[9] Interestingly, in the current work both the $(X, SiAl_4^-) \rightarrow (X, SiAl_4)$ and the $(X, GeAl_4^-) \rightarrow (X, GeAl_4)$ transitions are relatively sharp. These observations agree well with the relatively small geometry changes between the anionic and neutral molecules that contain Si and Ge centers. The planar structure of CAl_4^- was attributed to the occupation of the peripheral ligand–ligand bonding orbital (HOMO) by a single electron. When this electron is removed from the HOMO of CAl_4^- the corresponding neutral CAl_4 species becomes tetrahedral. In the case of $SiAl_4^-$ and $GeAl_4^-$, the peripheral ligand–ligand bond is no longer the HOMO, but the HOMO-2 ($4a_1$), which remains doubly occupied in both the anion and neutral ground states (Figure 3). Feature B in the photoelectron spectra corresponds to the removal of an electron from this peripheral bond, and the broad nature of feature B is consistent with the bonding nature of this orbital. Therefore, it is understandable that the neutral $SiAl_4$ and $GeAl_4$ compounds remain planar, unlike their lighter congener, CAl_4, which is tetrahedral. These results again reinforce the concept and importance of the ligand–ligand bonding in the stabilization of the planar structures in tetracoordinate C, Si, and Ge species.

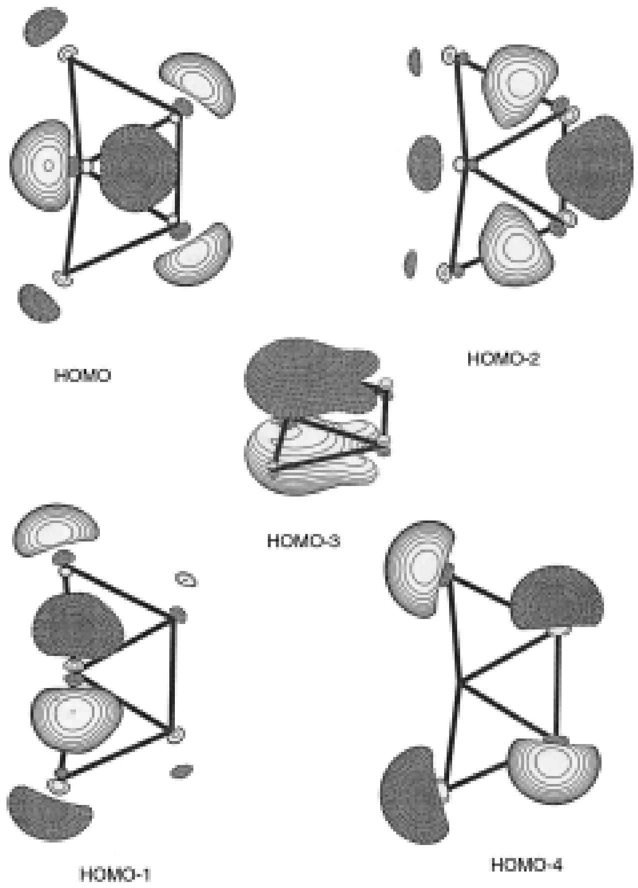

Figure 3. Molecular orbital diagram[16] showing the HOMO ($5a_1$), HOMO-1 ($3b_2$), HOMO-2 ($4a_1$), HOMO-3 ($1b_1$), and HOMO-4 ($2b_2$) of $SiAl_4^-$. Note that the ligand–ligand bonding MO is the HOMO-2 ($4a_1$), and not the HOMO as in CAl_4^-.[9]

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[1] R. Hoffmann, R. W. Alder, C. F. Wilcox, Jr, *J. Am. Chem. Soc.* **1970**, *92*, 4992.

[2] A. Streitwieser, S. M. Bachrach, A. Dorigo, P. v. R. Schleyer in *Lithium Chemistry: A Theoretical and Experimental Overview* (Eds.: A.-M. Sapse, P. von R. Schleyer), Wiley, New York, **1995**, p. 1.

[3] W. Luef, R. Keese, *Adv. Strain Org. Chem.* **1993**, *3*, 229.

[4] D. R. Rasmussen, L. Radom, *Angew. Chem.* **1999**, *111*, 3052; *Angew. Chem. Int. Ed.* **1999**, *38*, 2876.

[5] D. Rottger, G. Erker, *Angew. Chem.* **1997**, *109*, 840; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 812.

[6] D. Rottger, G. Erker, R. Frohlich, M. Grehl, S. Silverio, I. Hyla-Kryspin, R. Gleiter, *J. Am. Chem. Soc.* **1995**, *117*, 10503.

[7] A. I. Boldyrev, P. v. R. Schleyer, R. Keese, *Mendeleev Commun.* **1992**, 93.

[8] M. Aldoshin, O. A. D'yachenko, L. O. Atovmyan, A. N. Chekhov, M. I. Al'yanov, *Koord. Chem.* **1980**, *6*, 936.

[9] X. Li, L. S. Wang, A. I. Boldyrev, J. Simons, *J. Am. Chem. Soc.* **1999**, *121*, 6033.

[10] P. von R. Schleyer, A. I. Boldyrev, *J. Chem. Soc. Chem. Commun.* **1991**, 1536.

[11] A. I. Boldyrev, J. Simons, *J. Am. Chem. Soc.* **1998**, *120*, 7967.

1433-7851/00/3918-3309 $ 17.50+.50/0

[12] L. S. Wang, H. S. Cheng, J. Fan, *J. Chem. Phys.* **1995**, *102*, 9480.
[13] L. S. Wang, H. Wu in *Advances in Metal and Semiconductor Clusters. IV. Cluster Materials* (Ed.: M. A. Duncan), JAI, Greenwich, **1998**, pp. 299–343.
[14] We initially optimized the geometries and calculated the frequencies of $SiAl_4$, $GeAl_4$, $SiAl_4^-$, and $GeAl_4^-$ using analytical gradients with polarized split-valence basis sets (6-311 + G*) and a hybrid method known in the literature as B3LYP. Then we refined geometries and calculated frequencies at the second order Møller–Plesset perturbation theory (MP2) level. The energies of the lowest-energy structures were refined using the coupled-cluster (CCSD(T)) method and the more extended 6-311 + G(2df) basis sets. The VDEs and the first ADEs of $SiAl_4^-$, and $GeAl_4^-$ were calculated using the CCSD(T)/6-311 + G(2df) method. All the core electrons were kept frozen in the treatment of the electron correlation at the MP2 and CCSD(T) levels of theory.
[15] Gaussian 98, Revision A.7, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Lui, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**).
[16] The MO pictures were generated by using the MOLDEN3.4 program, G. Schaftenaar, MOLDEN3.4, CAOS/CAMM Center, The Netherlands, **1998**.

Control of Architecture in Block-Copolymer Vesicles**

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It has been known for some years that highly asymmetric amphiphilic block copolymers can self-assemble in solution to form crew-cut aggregates of an extremely wide range of morphologies.[1] The various morphologies include spheres, rods, bicontinuous structures, lamellae, vesicles, tubes, large compound vesicles (LCVs), hexagonally packed hollow hoops (HHHs), large compound micelles (LCMs), and many others. In such aggregates, the relatively long block forms the core, while the short one forms the corona. A number of other groups have also studied block-copolymer aggregates of various morphologies in recent years.[2, 3] The appeal of this field is, in part, because of the many potential applications of these nano-sized structures with their different morphologies, and in part academic curiosity.

Among the various morphologies, vesicles, including liposomes,[4] are of special interest because of their potential application as encapsulation agents. However the stability of liposomes has been a concern because of the high mobility of the component molecules under ambient conditions; therefore, many attempts have been made to stabilize these liposomes. As polymers have higher stability and lower mobility than small–molecule amphiphilies most of these stabilization strategies consist of the polymerization of the liposomes or the addition of polymeric materials to the liposomes.

Block-copolymer vesicles can be equilibrium structures under some conditions, but can also be kinetically frozen during preparation.[5] The block-copolymer vesicles are robust[3] and are very stable (samples have remained unchanged since 1997) in aqueous solution.[5] Because the studies on block-copolymer vesicles are still in the early stages, only a few attempts at encapsulation have been made.[3, 6]

To utilize block-copolymer vesicles in any given application, the precise control of vesicular parameters, such as vesicle size, wall thickness, number of walls, and space between the walls, is crucial. In our previous studies on the phase diagrams of block-copolymer systems we found that under some conditions the vesicles can be under thermodynamic control.[5] It is believed that the parameters which control the aggregate morphologies, that is the core chain stretching, interfacial tension, and corona repulsion, are also responsible for the control of the vesicular architecture. Thus, variation of these factors allows the properties of the vesicles to be tuned.[1]

A special type of vesicle, the so-called dense "onions", which are found in bulk block-copolymer blends were reported over a decade ago.[7] In block-copolymer solutions, onionlike micelles have been prepared by the stepwise aggregation of two diblocks, first AB and then BC.[8] Onion-like structures have also been reported in small molecule surfactant systems.[9] Recently, it was found that shear can induce the formation of onions from a lamella phase in surfactant systems.[10] By the same strategy, onionlike structures could also be formed in Pluronic systems,[11] and, very recently, onions were prepared from block-copolymer solutions.[12]

Herein we report a new morphology for block copolymers in solution, this consists of concentric vesicles with uniform spacing between the walls; we also describe the preparation in solution of multi-lamella onions in which there is no spacing between the walls, and discuss the control of these morphologies in the context of the other observed vesicular architectures (see Table 1).[1, 5, 13]. Our understanding of this subject is still qualitative, but the evidence obtained suggests that one can exercise control over a variety of vesicular morphologies. Noteworthy is that equally spaced concentric vesicles have been observed in small molecule amphiphiles.[4, 9]

Figure 1 shows concentric vesicles with uniform spaces between the walls, which we refer to as "onions with spaces". From the shadow of the vesicular structures seen by transition electron microscopy (TEM) observation (not shown here),

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