Inorg. Chem. **2002**, *41*, 2795–2798

Inorganic Chemistry

Article

Ab Initio Structure of the $(Na_2[CAl_4])_2$ Dimer. Next Step Toward Solid Materials Containing Tetracoordinate Planar Carbon

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Received November 30, 2001

We performed ab initio calculations on the $(Na_2[CAl_4])_2$ dimer in order to test if the two CAl_4^{2-} groups react to form the more stable dimeric structure, or if the two CAl_4^{2-} groups remain separated in a true dimeric structure. Working at the B3LYP/6-311+G* level of theory (previously found to be satisfactory in our earlier calculations with CAl_4^- and $Na[CAl_4]^-$), we established that structures with the C–C bond are higher in energy than the structures with two isolated structural CAl_4^- units separated by more than 5 Å with their structural and electronic integrity preserved. However, alternative structures involving reaction between two CAl_4^{2-} groups forming a $C_2Al_8^{4-}$ cluster without the C–C bond are higher in energy, but they are still competitive with the true dimeric structure. While we found alternative structures of $Na_4C_2Al_8$ with the energy comparable to that of the true dimeric structure, we hope that the solid ionic salt with the pentaatomic tetracoordinate planar carbon $[CAl_4]^{2-}$ building block can be synthesized.

I. Introduction

There have been substantial efforts described in the literature to design anti-van't Hoff/LeBel compounds containing tetracoordinate-planar-carbon (TPC) molecules.[1−4] We have been concentrating on small five-atomic species, the smallest molecules capable of containing a TPC, in which the bonding of the central carbon atom with its four ligands is easily traced. Furthermore, planarity in these species is not enforced by their molecular architecture, but rather by their intrinsic and unique electronic structure. On the basis of a simple molecular orbital picture, we found a general rule for achieving planarity in pentaatomic species composed of a first-row central atom and four second- or third-row ligand atoms: such species should possess 17- or 18-valence electrons.[5−11] Planarity of these species is achieved through a four-center, peripheral ligand−ligand bonding interaction in the highest occupied molecular orbital (HOMO).

The purpose of this work is to explore the possibility of designing new bulk solid materials containing pentaatomic TPC species as the building block. We have previously established that the 17-valence-electron CAl_4^- is a TPC molecule,[9] in which its ligand−ligand bonding HOMO is singly occupied. When the extra electron is detached, the neutral 16-valence-electron CAl_4 becomes tetrahedral.[9] The CAl_4^- anion, being electronically open-shell, is expected to be able to accept one more electron into its four-center ligand−ligand bonding HOMO, forming a closed-shell, that is, the 18-valence-electron dianion: CAl_4^{2-}. In our previous work,[11] we reported the first experimental salt-stabilized TPC realization of such a dianion, $Na^+[CAl_4^{2-}]$, and a theoretical investigation of this anion and the neutral $(Na^+)_2[CAl_4^{2-}]$ species. We confirmed that the TPC species, CAl_4^{2-}, can indeed maintain its structural and electronic integrity in the presence of one or two countercations. Although the four-center bond is peripheral, its structure is preserved with the influence of one or two cations. These findings represent the first step toward the realization of bulk materials based on crystal structural units composed of a new building block,

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10.1021/ic0112241 CCC: $22.00

the TPC dianion, [CAl_4^{2-}]. However, there is a paramount question that still needs to be addressed before experimental search for solid $M_2[CAl_4]$ (M = alkali metals, NH_4, Cu, Ag, Au) materials can be launched: do two CAl_4^{2-} groups react to form a carbon−carbon bond or do they not react to form a carbon−carbon bond in the C_2 unit? To make sure that these inquiries are addressed, we performed ab initio calculations; these demonstrate that the most stable structure is the true $(Na_2[CAl_4])_2$ dimer. These two structural CAl_4^{2-} units do not react with each other, and the CAl_4^{2-} building blocks preserve their integrity and planarity.

II. Theoretical Methods

In our previous treatment of CAl_4^{-} [9] and $Na^+[CAl_4^{-2}]$,[11] we used three sophisticated theoretical methods: a hybrid method that included a mixture of Hartree−Fock exchange with density functional exchange-correlation known in the literature as B3LYP,[12−14] the second-order Møller−Plesset Perturbation Theory (MP2) level, and the coupled cluster method (CCSD(T)) level of theory all with the 6-311+G* split-valent basis sets.[15−17] The optimized geometries, harmonic frequencies, and relative energies of the alternative structures were found in a reasonable agreement at all three levels of theory. Taking into account the size of the system, we limited our calculations to the only B3YP/6-311+G* level of theory. All calculations were performed using the Gaussian-98 program.[18]

III. Theoretical Results and Discussion

We started our search of the most stable structure of the $(Na_2[CAl_4])_2$ dimer with the assumption that two CAl_4^{2-} planar structure fragments do not react. The structure I (D_{4h}, $^1A_{1g}$) shown in Figure 1A was found to be a true minimum at the B3LYP/6-311+G* level of theory. Its calculated molecular properties are presented in Table 1. The CAl_4^{2-} fragments are essentially planar with the carbon−carbon distance 5.05 Å, clearly showing the absence of the bond between carbon atoms. The carbon−aluminum bonds (1.960 Å) on the other side are quite close to the carbon−aluminum bonds in the isolated CAl_4^{2-} dianion (1.98) and in the gas-phase Na^+[CAl_4^{2-}] salt anion (1.95 and 2.01 Å) calculated previously[11] at the B3LYP/6-311+G* level of theory. Four sodium cations are located between two dianions and thus keep the whole structure together. Structure I has some strain energy due to some distortion in the planarity of the CAl_4^{2-} group, because the C···C distance (5.05 Å) is larger than the Al···Al′ distance (4.33 Å). At the B3LYP/6-311+G* level of theory, the dissociation energy of the $(Na_2[CAl_4])_2$ dimer into two $Na_2[CAl_4]$ monomers was found to be 33.3 kcal/mol. Bonding in structure I is highly ionic between Na^+ and CAl_4^{2-} structural units (Table 1), but it is more covalent inside of the dianion. Similar to the previous study of the gas-phase $Na[CAl_4]^-$ and $Na_2[CAl_4]$ species, sodium cations in the dimer are coordinated to the peripheral bond of the dianion without destroying it, rather than coordinated to the more electronegative central carbon atoms. This is rather an unusual phenomenon in chemical bonding.

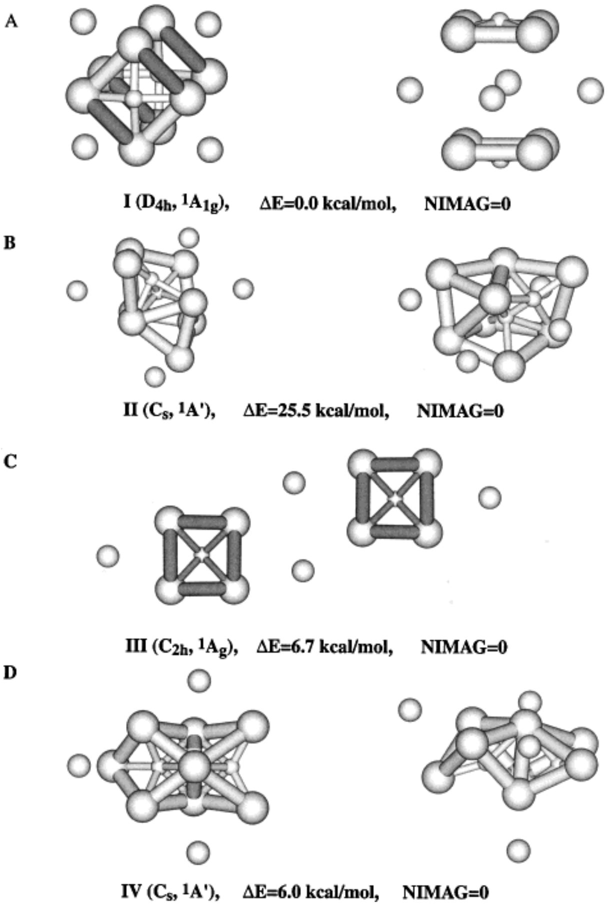

Figure 1. Optimized alternative local minimum structures of $Na_4C_2Al_8$ at the B3LYP/6-311+G* level of theory.

When we shortened the carbon−carbon distance in structure I of the $(Na_2[CAl_4])_2$ dimer up to the value 1.5 Å and reoptimized the structure preserving the D_{4h} symmetry, we found the resulting structure is a seventh order saddle point and it is 68.8 kcal/mol higher in energy than structure I. We optimized geometry without any symmetry restriction, and the optimized structure II (Figure 1B) was found to be a local minimum with a short carbon−carbon distance (1.43 Å), clearly showing the presence of the C−C bond. However,

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Table 1. Calculated Molecular Properties of the $(Na_2CAl_4)_2$ Structure

properties	$(Na_2CAl_4)_2$ I (D_{4h}, $^1A_{1g}$)	properties[a]	$(Na_2CAl_4)_2$ I (D_{4h}, $^1A_{1g}$)	properties[a]	$(Na_2CAl_4)_2$ I (D_{4h}, $^1A_{1g}$)
E_{tot}, au	−2665.14463	$\omega_1(a_{1g})$, cm^{-1}	452 (0.0)	$\omega_{15}(b_{1u})$, cm^{-1}	310 (0.0)
R(C−Al), Å	1.960	$\omega_2(a_{1g})$, cm^{-1}	246 (0.0)	$\omega_{16}(b_{1u})$, cm^{-1}	110 (0.0)
R(Al−Al), Å	2.725	$\omega_3(a_{1g})$, cm^{-1}	152 (0.0)	$\omega_{17}(b_{2u})$, cm^{-1}	274 (0.0)
R(C···C′), Å	5.045	$\omega_4(a_{1g})$, cm^{-1}	55 (0.0)	$\omega_{18}(b_{2u})$, cm^{-1}	105 (0.0)
R(Al···Al′), Å	4.338	$\omega_5(a_{2g})$, cm^{-1}	87 (0.0)	$\omega_{19}(e_g)$, cm^{-1}	770 (0.0)
R(Na−Al), Å	3.207	$\omega_6(a_{1u})$, cm^{-1}	55 (0.0)	$\omega_{20}(e_g)$, cm^{-1}	229 (0.0)
R(Na−Na), Å	4.659	$\omega_7(a_{2u})$, cm^{-1}	449 (0.0)	$\omega_{21}(e_g)$, cm^{-1}	133 (0.0)
∠Al−C−Al	88.1°	$\omega_8(a_{2u})$, cm^{-1}	199 (70.2)	$\omega_{22}(e_g)$, cm^{-1}	55 (0.0)
∠Na−C−Na	68.3°	$\omega_9(a_{2u})$, cm^{-1}	152 (29.3)	$\omega_{23}(e_u)$, cm^{-1}	791 (239.7)
Q^{NPA}(C),[b] e	−2.647	$\omega_{10}(b_{1g})$, cm^{-1}	285 (0.0)	$\omega_{24}(e_u)$, cm^{-1}	236 (5.6)
Q^{NPA}(Al),[b] e	+0.248	$\omega_{11}(b_{1g})$, cm^{-1}	126 (0.0)	$\omega_{25}(e_u)$, cm^{-1}	153 (32.0)
Q^{NPA}(Na),[b] e	+0.828	$\omega_{12}(b_{2g})$, cm^{-1}	319 (0.0)	$\omega_{26}(e_u)$, cm^{-1}	99 (30.7)
		$\omega_{13}(b_{2g})$, cm^{-1}	137 (0.0)	$\omega_{27}(e_u)$, cm^{-1}	62 (1.6)
		$\omega_{14}(b_{2g})$, cm^{-1}	67 (0.0)		

[a] Infrared intensities (in km/mol) are given in parentheses. [b] Effective atomic charges calculated using natural population analysis incorporated in *Gaussian 98.*

being a minimum, structure II is still substantially higher in energy (by 25.5 kcal/mol) than the true dimeric structure I.

On the basis of these calculations, we concluded that forming the C−C bond is not a favorable process for the stoichiometry $Na_4C_2Al_8$. We should expect that, when the number of aluminum atoms relative to the number of carbon atoms is large enough, the C_2^{x-} group is not stable inside of the aluminum cluster and would dissociate into two atomic carbon anions. While a large number of binary and ternary metal carbides with C_2^{2-} are known,[19,20] particularly in carbides of electropositive elements (alkali, alkali earth, and rare earth), aluminum forms a stoichiometric carbide compound (Al_4C_3), which reacts with water to produce methane.[19,20] Thus, the aluminum carbide contains discrete carbon atoms, which can be viewed as C^{4-}, rather than the familiar C_2^{2-}. Therefore, our theoretical results and the absence of the aluminum carbide with the C_2^{2-} unit provide us evidence that in the solid salt with the stoichiometry Na_2CAl_4 the CAl_4^{2-} groups will not react with each other with the formation of the structural C_2^{2-} unit.

We also studied structures with two isolated CAl_4^{2-} structural units located in the same plane. Structure III (Figure 1C) was found to be a local minimum 6.7 kcal/mol higher in energy than the most stable structure I, showing importance of the high coordination number for cations (Na^+) and anions (CAl_4^{2-}).

Next, we studied a series of structures formed by a reaction between CAl_4^{2-} structural groups without the formation of the C−C bonds. In structure IV (Figure 1D), we maximized the coordination number (resulting number is 5) for both C atoms and allowed carbon atoms to have two bridged aluminum atoms. Geometry optimization without any symmetry restrictions yields structure IV (Figure 1D), which was found to be a local minimum, and it being only 6.0 kcal/mol higher in energy than structure I shows that alternative structures containing C_2Al_8 cluster are competitors to the true dimeric structure.

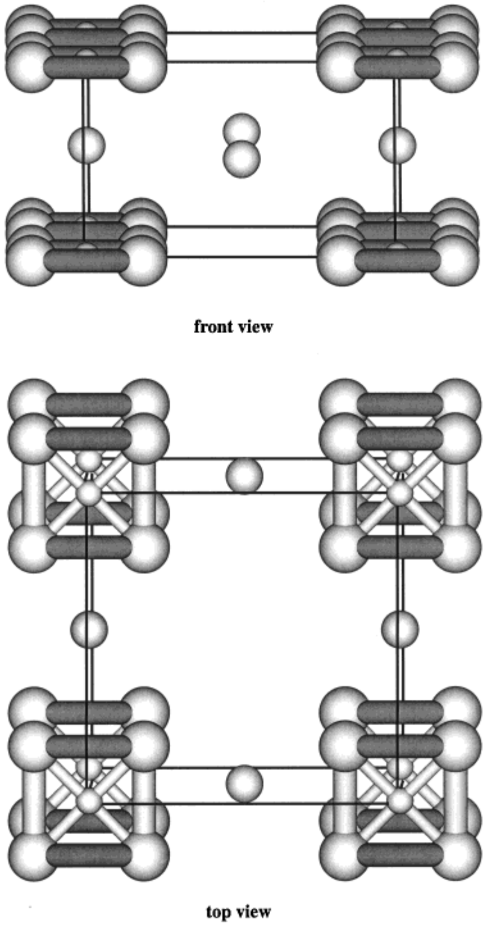

Figure 2. Proposed crystal structure for the $Na_2[CAl_4]$ stoichiometry.

We optimized geometries for many other alternative structures of $Na_4C_2Al_8$ and found all of them to be higher in energy than structures I and IV, and therefore, we will not discuss them as a part of this study.

While we found alternative structures of $Na_4C_2Al_8$ with energy comparable to the true dimeric structure, we believe that still there is hope to make crystal salt structure with the stoichiometry Na_2CAl_4 which may have a structure shown in Figure 2. Our hope is based on the further contribution in the stabilization of the salt structure from the lattice energy and the reduction of the strain energy in CAl_4^{2-} in the three-

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dimensional structure. We hope that this work will stimulate experimental efforts to synthesize the first ionic solid salt containing the pentaatomic CAl_4^{2-} planar carbon unit.

IV. Conclusions

On the basis of ab initio calculations performed for the $(Na_2[CAl_4])_2$ dimer, we found that the true dimeric structure is a minimum with the two CAl_4^{2-} separated groups. This structure is more favorable than alternative structures with the formation of the C−C bond. These theoretical results with the experimentally known fact that aluminum and carbon form the Al_4C_3 carbide composed of Al^{3+} and C^{4-} provide us hope that the solid ionic salt with the $Na_2[CAl_4]$ stoichiometry can be synthesized, which will be the first solid containing the pentaatomic tetracoordinate planar carbon (CAl_4^{2-}) building block.

Acknowledgment. The theoretical work was done at Utah State University and supported by the donors of the Petroleum Research Fund (ACS-PRF# 35255-AC6), administered by the American Chemical Society.

IC0112241