

Pentaatomic Tetracoordinate Planar Carbon, $[\text{CAI}_4]^{2-}$: A New Structural Unit and Its Salt Complexes**

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Since the pioneering theoretical formulation of hypothetical tetracoordinate planar carbon (TPC) molecules by Hoffmann et al. thirty years ago,^[1] there have been substantial research efforts to design new molecules that may contain tetracoordinate planar carbon.^[2–13] Schleyer et al.^[2–4] computationally tested and predicted a wide variety of candidate molecules for TPC, many of which were reviewed recently.^[4] Keese et al.^[6, 7] performed calculations on promising candidates and synthesized many such molecules. Radom et al.^[8, 9] performed calculations on a class of polycyclic hydrocarbons, called alkplanes, in which TPC can be achieved by steric constraints. A divanadium complex, characterized structurally by Cotton and Millar,^[10] is probably the first compound with a TPC atom. A variety of organometallic compounds, mostly containing elements of Groups 4 and 5, have since been reported by Erker, Gleiter, and co-workers to contain TPC.^[11–13]

Our efforts to design new TPC molecules have concentrated on small five-atom species, the smallest molecules that can contain a TPC atom, in which the bonding of the central carbon atom to its four ligands can be 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.^[14–16] Planarity of these species is achieved through a four-center peripheral ligand–ligand bonding interaction in their highest occupied molecular orbital (HOMO).

Here we discuss the possibility of designing new materials containing such pentaatomic TPC species as building blocks for bulk solid materials. We previously established that the 17-valence-electron CAI_4^- is a TPC molecule^[16] in which the ligand–ligand bonding HOMO is singly occupied. When the extra electron is detached, the 16-valence-electron neutral CAI_4 becomes tetrahedral. The CAI_4^- ion, with its open electronic shell, is thus expected to be able to accept one more electron into its four-center ligand–ligand bonding HOMO to generate the closed-shell, 18-valence-electron dianion CAI_4^{2-} . However, this doubly charged anion is not expected to be stable towards electron autodetachment in its isolated state due to strong Coulomb repulsion between the two extra electrons, analogous to the sulfate dianion SO_4^{2-} , which is well known to be unstable in the gas phase.^[17] One strategy to stabilize such a dianion is to provide it with a counterion, as we observed recently in a series of stable $\text{M}^+[\text{SO}_4^{2-}]$ species.^[18] Here we report the first experimental realization of such a salt-stabilized TPC dianion, namely, $\text{Na}^+[\text{CAI}_4^{2-}]$, and a theoretical investigation of this anion and the neutral $(\text{Na}^+)_2[\text{CAI}_4^{2-}]$ species. We confirm that the TPC species CAI_4^{2-} can indeed maintain its structural integrity in the presence of one or two counterions. These findings represent the first step towards the realization of bulk materials based on crystal structural units containing the TPC dianion $[\text{CAI}_4^{2-}]$ as a novel building block.

The experiment was performed with a magnetic-bottle photoelectron spectroscopy apparatus equipped with a laser vaporization source.^[19] We made NaCAI_4^- by laser vaporization of an Al/C/Na composite target containing 75% Al, 5% C, and 20% NaI by weight. Various Al_xC_y^- species and clusters containing Na and I were observed and analyzed by a time-of-flight mass spectrometer. The NaCAI_4^- ions were mass-selected and detached by a laser beam in the interaction zone of the magnetic-bottle photoelectron analyzer. Photoelectron spectra were measured at two detachment photon energies, 355 nm (3.496 eV) and 266 nm (4.661 eV), as shown in Figure 1. The electron energy resolution was better than 30 meV for 1 eV electrons.

In the theoretical investigation,^[20, 21] we studied extensively possible structures for $\text{Na}^+[\text{CAI}_4^{2-}]$ and $(\text{Na}^+)_2[\text{CAI}_4^{2-}]$. At the B3LYP/6-311+G* level of theory, the most stable structure for $\text{Na}^+[\text{CAI}_4^{2-}]$ was found to be planar with coordination of Na^+ to an edge of CAI_4^{2-} (Figure 2a). Two other structures, in which Na^+ is coordinated to a corner Al atom or directly to the C atom to form a square pyramid are first- and second-order saddle points lying 14.5 and 12.1 kcal mol⁻¹ higher in energy than the bidentate global-minimum structure, respectively. There is, however, another local minimum corresponding to a structure (Figure 2b), which can be viewed as exchanging the positions of Na^+ and one of the corner Al atoms in the ground-state structure. This isomer is 25.4 kcal mol⁻¹ higher in energy. When we exchanged Na and one of the bridged Al atoms in the ground-state structure, the resulting species collapsed into the global minimum upon optimization. For $(\text{Na}^+)_2[\text{CAI}_4^{2-}]$, the most stable structure is also planar with coordination of the two Na^+ ions to opposite edges of CAI_4^{2-} (Figure 2c). We found another low-lying stable isomer, which is also planar, but in

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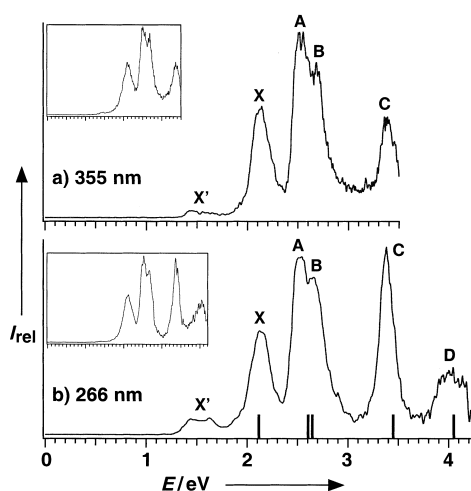


Figure 1. Photoelectron spectra of $\text{Na}^+[\text{CAI}_4]^{2-}$ at 355 nm (3.496 eV) and 266 nm (4.661 eV), plotted in increasing electron binding energy. The five major detachment channels observed are labeled (X, A, B, C, and D). The vertical bars in b) mark the calculated vertical electron detachment energies from the ground state of $\text{Na}^+[\text{CAI}_4]^{2-}$. The insets display spectra recorded with a slightly hotter source condition and show the disappearance of the X' feature, which was due to a higher energy isomer (see text). I_{rel} = relative electron intensity.

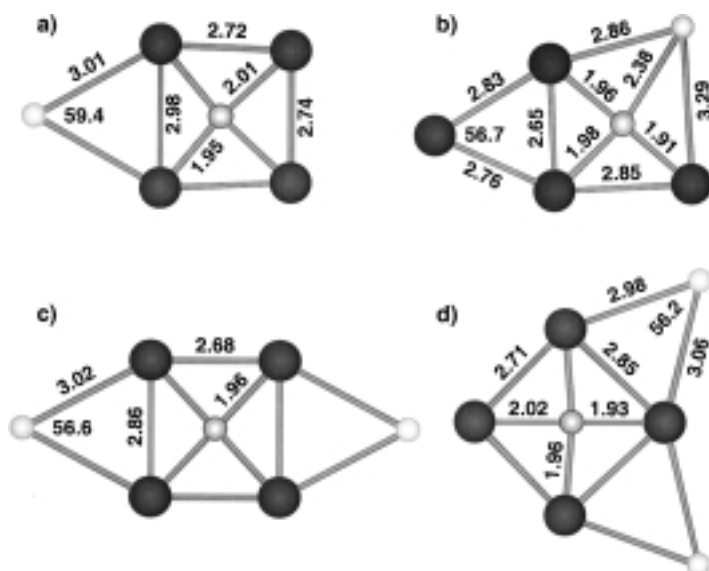


Figure 2. The global minima and low-lying isomers of $\text{Na}^+[\text{CAI}_4]^{2-}$ and $(\text{Na}^+)_2[\text{CAI}_4]^{2-}$ optimized at the B3LYP/6-311 + G* level of theory. a) and c) represent the global minimum structures for each species, whereas b) and d) are the corresponding low-lying isomers. The selected bond lengths are in Å and the bond angles in degrees.

which the two Na^+ ions are coordinated to adjoining edges of CAI_4^{2-} (Figure 2d). This isomer is 3.7 kcal mol⁻¹ higher in energy than the global minimum. The saddle point, corresponding to the transition state (barrier height -6.9 kcal mol⁻¹) on the intramolecular rearrangement from the structure of Figure 2d to that of Figure 2c, is a planar structure in which one Na^+ ion is coordinated to an edge and the other to a corner Al atom of CAI_4^{2-} . Two more structures with direct coordination of Na^+ to the carbon atom and to two Al atoms at opposite corners were also examined. Both structures are second-order saddle points and are 29.2 and 20.9 kcal mol⁻¹ higher in energy than the global minimum, respectively.

At the more sophisticated MP2/6-311 + G* level of theory, the structures shown in Figure 2 are slightly nonplanar, but the bond lengths and valence angles are essentially the same as those obtained at the B3LYP/6-311 + G* level. Moreover, the energy differences between the perfectly planar structures and the slightly nonplanar global-minimum structures were smaller than the differences in the zero-point energies. Therefore, the vibrationally averaged structures are all essentially planar. This slight nonplanarity is similar to that of the parent TPC anion CAI_4^- .^[16] In the interpretation of the experimental spectra, we used the planar C_{2v} structure of $\text{Na}^+[\text{CAI}_4^{2-}]$. At the highest level of theory (CCSD(T)/6-311 + G(2df)//MP2/6-311 + G*), the second isomer of $(\text{Na}^+)[\text{CAI}_4^{2-}]$ (Figure 2b) is 25.2 kcal mol⁻¹ higher in energy than the global-minimum structure (Figure 2a), and the second isomer of $(\text{Na}^+)_2[\text{CAI}_4^{2-}]$ (Figure 2d) is 4.0 kcal mol⁻¹ higher in energy than the global-minimum structure (Figure 2c).

The 355-nm spectrum of NaCAI_4^- revealed four major features (X, A–C) (Figure 1 a), whereby the A and B features are closely spaced. At 266 nm, an additional feature (D) was observed (Figure 1 b). The weak feature near 1.5 eV (X') was assigned to the second isomer of NaCAI_4^- . The insets in Figure 1 display a set of data recorded with a slightly hotter source; here the X' feature was almost completely eliminated. This observation is consistent with the isomer assignment, because the higher energy isomer may isomerize to the ground-state structure more readily under the slightly hotter conditions. The measured adiabatic and vertical electron binding energies (ADEs and VDEs, respectively) for the global minimum structure and the second isomer are given in Table 1. The theoretical results for the global minimum are in excellent agreement with the experimental ADEs and VDEs (Figure 1 b), and this confirms that we have indeed made the $\text{Na}^+[\text{CAI}_4^{2-}]$ charge-transfer salt containing the TPC dianion CAI_4^{2-} . The calculated VDE for the second isomer was 1.70 eV, which agrees well with the X' feature near 1.5 eV and confirms our assignment for the second isomer. The features of higher binding energy for the second isomers were probably buried in the spectral features of the ground-state anion (Figure 1).

Bonding in $\text{Na}^+[\text{CAI}_4^{2-}]$ can be understood by analyzing the molecular orbitals and calculated effective atomic charges. The interaction between Na^+ and CAI_4^{2-} is mostly ionic. The representative atomic charges (NPA) were calculated to be: $Q(\text{Na}) = +0.57 |e|$, $Q(\text{bridged Al}) = +0.15 |e|$, $Q(\text{corner Al}) = +0.32 |e|$, and $Q(\text{C}) = -2.51 |e|$ for the global minimum of $\text{Na}^+[\text{CAI}_4^{2-}]$ (Figure 2a). On the basis of these charge distributions, one might expect that the pyramidal structure should be the most stable, because the positively charged sodium atom is supposed to be favorably coordinated directly to the most electronegative carbon atom. However, the pyramidal structure is much less stable and is not even a local minimum. Insight into this paradox can be obtained by examining the molecular orbitals of $\text{Na}^+[\text{CAI}_4^{2-}]$. Figure 3 shows its four highest orbitals: the ligand–ligand bonding HOMO (5a₁) and three nonbonding ligand lone-pair orbitals (3b₂, 4a₁, 2b₂). The Na^+ ion is actually coordinated to the electron density that corresponds to the ligand–ligand

Table 1. Experimental and theoretical vertical (VDE) and adiabatic (ADE) electron detachment energies for the ground state and the low-lying isomer of $\text{Na}^+[\text{CAL}_4^{2-}]$.

State	Experimental VDE [eV]	Experimental ADE [eV]	Detachment channel ^[a]	Theoretical ^[b] VDE [eV]	Theoretical ^[c] ADE [eV]
Ground state of $\text{Na}^+[\text{CAL}_4^{2-}]$ (Figure 2a)					
X	2.12 (0.03)	2.02 (0.06)	$5a_1$ (2A_1)	2.11 (0.86)	2.00
A	2.54 (0.04)	2.65 (0.03)	$3b_2$ (2B_2)	2.62 (0.84)	–
B	2.67 (0.04)	–	$4a_1$ (2A_1)	2.63 (0.85)	–
C	3.38 (0.03)	3.28 (0.06)	$2b_2$ (2B_2)	3.47 (0.83)	–
D	4.04 (0.08)	3.88 (0.06)	$1b_1$ (2B_1)	4.07 (0.86)	–
Low-lying isomer of $\text{Na}^+[\text{CAL}_4^{2-}]$ (Figure 2b)					
X'	≈ 1.5	≈ 1.4	$8a'$ (${}^2A'$)	1.70 (0.86)	–
A'	–	–	$7a'$ (${}^2A'$)	2.26 (0.84)	–
B'	–	–	$6a'$ (${}^2A'$)	2.89 (0.84)	–
C'	–	–	$1a''$ (${}^2A''$)	3.71 (0.85)	–
D'	–	–	$5a'$ (${}^2A'$)	3.87 (0.80)	–

[a] The final state of $\text{Na}^+[\text{CAL}_4^{2-}]$ is given in parentheses. See Figure 3 for pictures of the orbitals of the ground-state structure. [b] All data are at the OVGF/6-311+G(2df)//MP2/6-311+G* level of theory. The pole strength is given in parentheses. [c] At the CCSD(T)/6-311+G(2df)//MP2/6-311+G* level of theory.

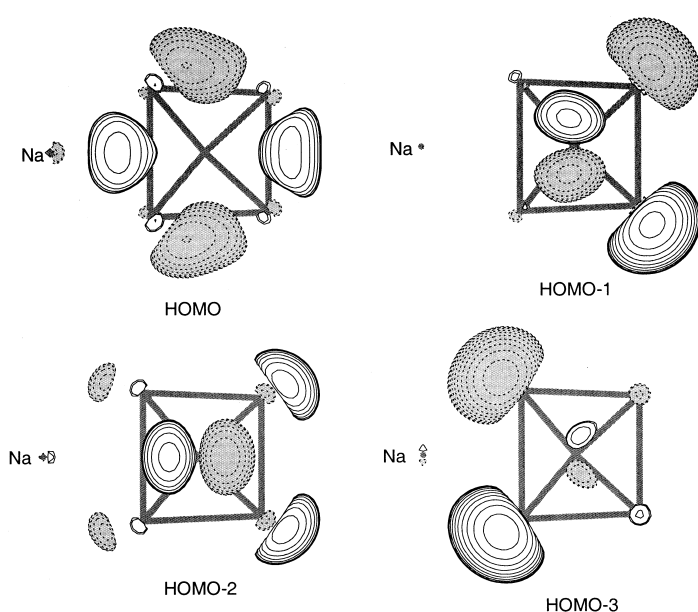


Figure 3. The four highest valence molecular orbitals^[22] of $\text{Na}^+[\text{CAL}_4^{2-}]$ (C_{2v} , 1A_1): HOMO ($5a_1$), HOMO-1 ($3b_2$), HOMO-2 ($4a_1$), HOMO-3 ($2b_2$).

peripheral bond with only minor perturbation to the TPC unit. Therefore, for this molecule we need to consider not only the effective atomic charges, but also peripheral electron density, which is not represented by the atomic charges. The fact that the four-center peripheral ligand–ligand bond and the TPC unit in both $\text{Na}^+[\text{CAL}_4^{2-}]$ and $(\text{Na}^+)_2[\text{CAL}_4^{2-}]$ can maintain their integrity is remarkable and suggests that there is considerable potential that bulk solid materials containing $[\text{CAL}_4^{2-}]$ as a new chemical structural unit may be prepared with the composition $(\text{M}^+)_2[\text{CAL}_4^{2-}]$.

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 [20] We initially optimized geometries and calculated frequencies of $\text{Na}^+[\text{CAL}_4^{2-}]$ and $(\text{Na}^+)_2[\text{CAL}_4^{2-}]$ by 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 by using the coupled-cluster (CCSD(T)) method and the more extended 6-311+G(2df) basis sets. The first ADE of $\text{Na}^+[\text{CAL}_4^{2-}]$ were calculated by using the CCSD(T)/6-311+G(2df) method. The VDEs were calculated by the outer valence green function method (OVGF) with 6-311+G(2df) basis sets. All core electrons were kept frozen in treating the electron correlation at the MP2, CCSD(T), and OVGF levels of theory.
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