Bonding in an Unusual Nickel Carbide

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Carbides, Molecular Orbitals, Electronic Structure, Metal Carbides, Square-Planar Carbon

The bonding in an unusual nickel carbide polymer network synthesized by Musanke and Jeitschko is analyzed using qualitative, band-structure calculations in the framework of extended Hückel tight-binding theory. The carbide features infinite, one-dimensional, vertex-sharing chains of Ni squares. Each square is centered by a carbon and flanked by C_2 units.

In this electron-rich polymer, the Ni atoms act as electron acceptors through their s and p orbitals. The orbital interaction schemes reveal that there is little Ni-Ni bonding and essentially no Ni to C_2 back-donation. Molecular orbital interaction diagrams of some molecular models are used to describe the bonding in $^1_\infty[Ni_3C_5]^{8-}$.

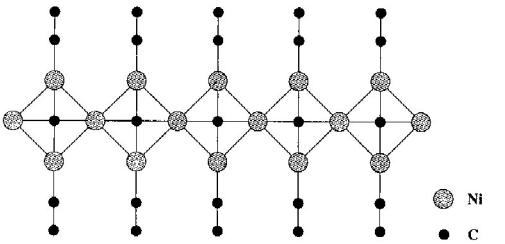
We also discuss the stability of the planar building block of the polymer, $(CNi_4)^{4-}$ (which resembles planar CH_4) with respect to a "tetrahedral" alternative and we do so for the extended $^1_\infty[Ni_3C]^{4-}$ and $^1_\infty[Ni_3C_5]^{8-}$ chains. In each model case the tetrahedral alternative is favored, and there is no sign of stabilization of a crucial CL_4 orbital. Such stabilization is partially achieved through bonding to two Ca axial to the C in the center of the Ni_4 ring, but it takes the entire inter-chain calcium network to effect the observed stabilization.

1. The Carbide Structure

In the solid state structures of binary and ternary transition metal carbide compounds, carbon atoms (or ions, no implication is made as to their ionicity) exhibit a variety of bonding modes, ranging from isolated C atoms to C_2 and C_3 groups, or combinations of these [1 - 24]. Most frequently, carbides contain C_1 and C_2 moieties in the solid state, spanning a remarkable range of bond lengths (roughly that of all organic C-C bonds). In many of these structures one also finds transition metal-carbon networks of varying dimensionality.

Recently, Musanke and Jeitschko synthesized a unique compound, $Ca_4Ni_3C_5$ [16]. In its structure one finds the one-dimensional $^1_\infty[Ni_3C_5]^{8-}$ sublattice depicted in a slightly idealized geometry in **1**.

This one-dimensional, organometallic structure can be viewed as built from corner-sharing Ni_4C squares, with terminal C_2 groups bonded to each edge Ni atom. The central carbide atom is surrounded by four Ni atoms in an approximately



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square-planar geometry. To put it mildly, this is highly unusual for a four-coordinated C center. The Ni-$C_{central}$ bond lengths are 1.89 and 1.83 Å respectively (the longer bond being along the direction of the chain), on the short side of organometallic Ni-C bond lengths. The Ni-Ni distance is 2.63 Å, within the range of Ni-Ni single bonds. The distances between the outer Ni's and the nearest carbon of the terminal C_2 groups (hereafter denoted as Ni-C_2) are also fairly short, 1.86 Å. These terminal C_2 groups have a C-C bond length (1.21 Å) corresponding to a typical C-C triple bond. This is among the shortest C-C bonds found in transition metal carbide compounds, comparable to that found in CaC_2 [1, 4, 13].

If we take the formal charge of Ca to be +2, the polymeric substructure as shown in **1** can be

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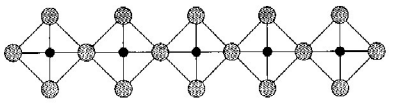
formally described as $^{1}_{\infty}[Ni_3C(C_2)_2]^{8-}$. Since the terminal C_2 groups appear to be triply-bonded, it is reasonable to view them as C_2^{2-}. If we take the Ni atoms as neutral (this is just an assumption!), the central carbon atom is formally C^{4-}. The compound might then be written as $(Ca^{2+})_4Ni_3(C^{4-})(C_2^{2-})_2$, and the infinite, one-dimensional, organometallic substructure is $[Ni_3C(C_2)_2]^{8-}$.

The remarkable structure raises many questions. What is the nature of the bonding of the four-coordinate, planar carbon atom in **1**, and why is it stable? How do the C_2^{2-} groups interact with the organometallic polymer core? How is the bonding in the extended structure related to its molecular fragments? Does the formal charge assignment assumed by us above make sense? Finally, we would like to explore some structural alternatives to the planar structure **1**.

In this study we utilize molecular and tight-binding extended Hückel calculations [25 - 31] to study the bonding in **1** and in models for this structure. All computational details are given in the Appendix. Fragment molecular orbital (FMO) arguments [31 - 33] in conjunction with band structure results, are used to analyze the structure and bonding of this compound.

2. Building Up the Core Polymer

Let us begin our discussion with some simpler structures from which we can build up our understanding of polymer **1**. A convenient fragmentation of **1** is to first strip off all terminal C_2^{2-} groups, leaving a one-dimensional $^{1}_{\infty}[Ni_3C]^{4-}$ polymer, shown in **2**.



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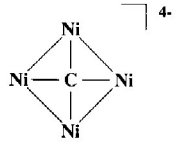
Going back further in this "retrotheoretical" line of analysis, we first look into the bonding in a hypothetical, molecular, square planar $(Ni_4C)^{4-}$, **3**, the basic, zero-dimensional, structural motif of the one-dimensional system.



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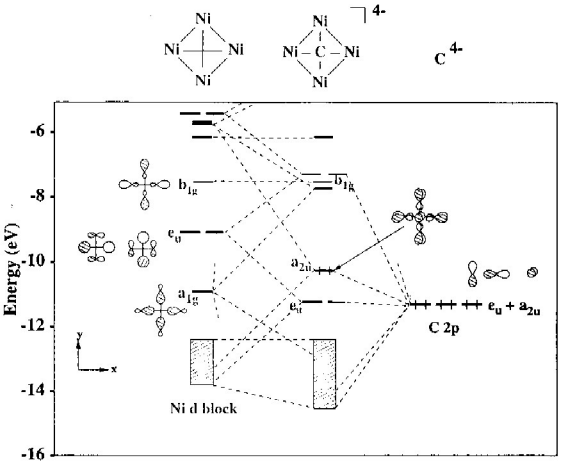


Fig. 1. An FMO diagram for molecular model $(Ni_4C)^{4-}$ (**3**).

In our calculations, all Ni-C bond lengths are slightly idealized, by being set to the same length (1.86 Å).

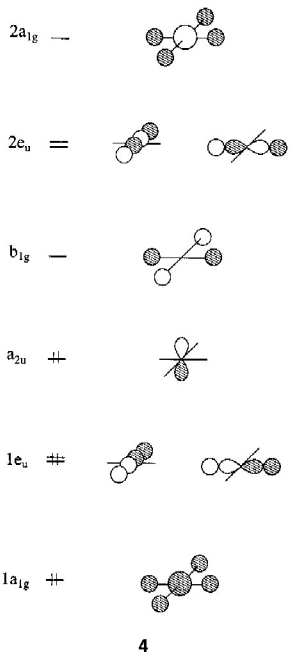
The bonding in the molecular fragment **3** can be approached through an interaction diagram between the C^{4-} ion and a square planar Ni_4 fragment, shown in Fig. 1.

A simplifying feature of the analysis is that the Ni 3d orbitals emerge quite low in energy, and the bonding with the carbon (here and in the polymeric structures to be examined) is accomplished mainly through Ni 4s and 4p orbitals. These form typical "cyclobutadienoid" symmetry-adapted combinations, some of which are shown at left in Fig. 1.

The main Ni-C interaction seen in Fig. 1 is between the C 2p orbitals and those cyclobutadienoid s and p orbital combinations on Ni_4. The C p_x and p_y orbital set (of e_u symmetry) interacts with the Ni s and p e_u orbital set (with slight d orbital admixture), resulting in the e_u molecular orbitals of **3**. The lower e_u pair coming from this interaction (at about –11.3 eV in Fig. 1) is mainly responsible for the Ni-C σ interaction (along with a lower lying a_{1g} orbital in the d-block). The C p_z orbital (a_{2u}) interacts with appropriate symmetry orbitals (3d and 4p) on the Ni_4 side. The resulting HOMO, a_{2u}, is mainly C p_z in character with some admixture of the Ni d orbitals. We will return to this crucial orbital soon. Interestingly, Ni_4C^{4-} is a closed-shell structure with a reasonable gap to some unfilled orbitals. Some of these are "dangling bonds", directed out

of the Ni square and likely to make such a cluster quite reactive.

What is the relationship of the orbitals of $(Ni_4C)^{4-}$ to those of hypothetical square-planar carbon in CH_4 or CR_4? The electronic structure of planar, tetracoordinate carbon has been analyzed in some detail over the years [32, 34 - 38]; the essential orbitals of D_{4h} CH_4 are shown in **4** below.



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Note the electron-deficient, three-center bonding in the lowest three orbitals ($1a_{1g}$ + $1e_u$), and the carbon p_z-based a_{2u} lone pair. The corresponding a_{2u} and e_u orbitals are apparent in Fig 1. There is an obvious resemblance in the bonding of D_{4h} CH_4 and $(Ni_4C)^{4-}$. And there is no hint of stabilization in the organometallic. The critical a_{2u} orbital is slightly destabilized (compared to a pure C p_z) because it is C-Ni antibonding; the corresponding bonding combination is Ni-d based and is thus located in the lower-energy d block. It appears that the antibonding mixing of Ni 3d (acting as a donor) into the C $2p_z$ overcomes the bonding with Ni 4p combinations (acting as an acceptor).

The electronic structure of the $(Ni_4C)^{4-}$ molecular fragment helps us to understand the bonding in the $^1_\infty[Ni_3C]^{4-}$ polymer. The juxtaposition of the band stucture of the polymer with the orbitals of the molecular subunit in Fig. 2 shows the similarity in

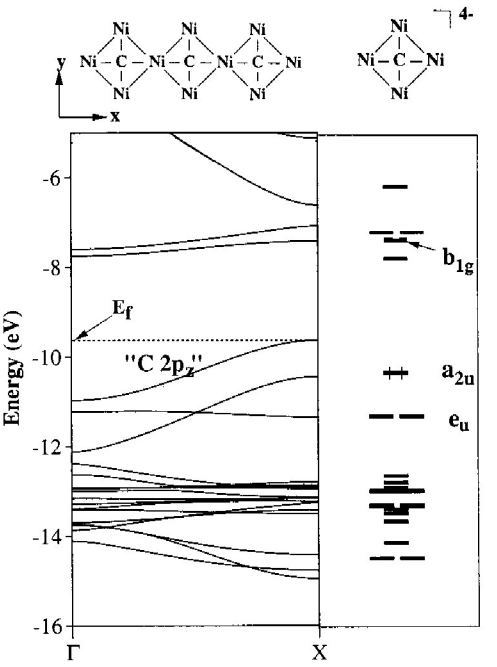


Fig. 2. Band structure of the model polymer $^1_\infty[Ni_3C]^{4-}$ (**2**). The horizontal dotted line denotes the Fermi level. At right is the molecular orbital energy diagram for $(Ni_4C)^{4-}$ (**3**).

the energy levels of the two systems. Note that there is one more Ni atom in the $(Ni_4C)^{4-}$ molecular fragment **3** than in the unit cell of the extended system $^1_\infty[Ni_3C]^{4-}$; thus there is one band less in the vertex-shared chain than there are molecular orbitals in the molecular fragment.

The Fermi level of the extended system is at –9.63 eV. The highest filled band (marked "C $2p_z$" in Fig. 2 corresponds to the aforementioned a_{2u} orbital in the $(Ni_4C)^{4-}$ fragment (mainly C $2p_z$, π antibonding between the central C and surrounding Ni atoms, as described above for the molecular fragment.) The next two bands (see Fig. 2) are related to the e_u set in the $(Ni_4C)^{4-}$ model (C p_x,p_y and Ni d). The composition of these three, high-lying bands is apparent from contributions of various orbitals to the DOS shown in Fig. 3.

The clump of relatively flat bands from –12.5 eV downward, generating the largest DOS peak in Fig. 3c, contains the Ni d bands. The band which is responsible for the Ni-C σ bonding is down low in energy and is not plotted in Fig. 2. As in the molecular model, the main factor holding the extended

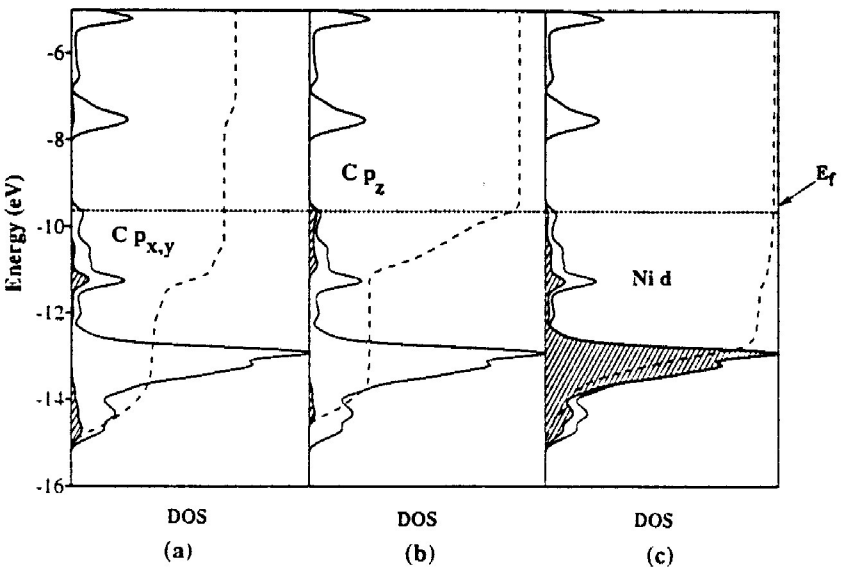


Fig. 3. DOS contributions (shaded areas) for $^1_\infty[Ni_3C]^{4-}$ (2) (a) C p_x and p_y orbitals; (b) C p_z orbital; and (c) all Ni d orbitals. The horizontal dashed lines denote the Fermi level, and the dotted curves are the integration of the DOS contributions.

system together is the mixing of 4s and 4p orbitals on Ni with C orbitals of appropriate symmetry.

Of course, square planar CH_4 is unstable relative to a preferred tetrahedral geometry. This instability is traceable to just the a_{2u} orbital we mentioned, completely nonbonding in the square planar CH_4 but part of a bonding combination in tetrahedral methane. Strategies for stabilizing square-planar, tetracoordinate carbon focus on this MO [34]. We hoped that the bonding in the extended system would stabilize the high lying a_{2u} orbital of square-planar carbon. But since the HOMO of the polymer, the main component of which is the C p_z orbital, lies actually slightly higher in energy than the pure C p_z orbital, the additional Ni-C p interaction in this case appears not be the driving force that stabilizes the planar structure.

A Mulliken population analysis on the $^1_\infty[Ni_3C]^{4-}$ extended system yields a computed net charge of –1.88 on the central C, –0.59 on the edge Ni, and –0.94 on the bridging Ni. In the model the Ni-C distances are assumed equal; the charge asymmetry is a function of the connectivity of the Ni's. The bridging or vertex-shared Ni atom is more negatively charged than the edge ones because of the charge transfer from two neighboring C^{4-} ions into the s and p orbitals of the former; the "side" Ni atoms have only one neighboring C^{4-}.

The average overlap populations of the two types of Ni-C bonds in the polymeric chain are essentially the same (0.54 and 0.52). The COOP plots (not shown here) indicate that only Ni-C bonding bands are filled, except for the top band which is C-Ni π antibonding. On the other hand, some Ni-Ni antibonding levels (at the top of the d bands) are occupied; thus the computed Ni-Ni bonding, despite the relatively short metal-metal separation (2.63 Å), is not strong—the net Ni-Ni overlap population is only 0.05. At the same Ni-Ni distance, a *bona fide* Ni-Ni single bond as in $Ni_2(CN)_6^{4-}$ [39, 40] has an overlap population of 0.23. The significantly smaller Ni-Ni overlap population in the polymer, despite the reasonably short Ni-Ni distance, reflects the fact that the Ni d block is completely filled. The non-zero Ni-Ni overlap population despite the fully filled d band is a result of the mixing of the Ni s and p orbitals into the Ni d band [41 - 43].

3. Square-Planar vs. Tetrahedral Models and Polymers

The question remains as to why the C atom is stable in its square-planar environment. As we noted, in the molecular $(Ni_4C)^{4-}$ model in Fig. 1 the a_{2u} orbital is in fact slightly higher in energy than the pure C p_z orbital of a_{2u} symmetry. Judging by just this orbital, there is no obvious rationale for the stability of the planar structure.

In fact, let's consider the following question: could there be other geometries that might be of comparable energy to the one observed? Clearly, a tetrahedral CH_4 is much more stable than its square-

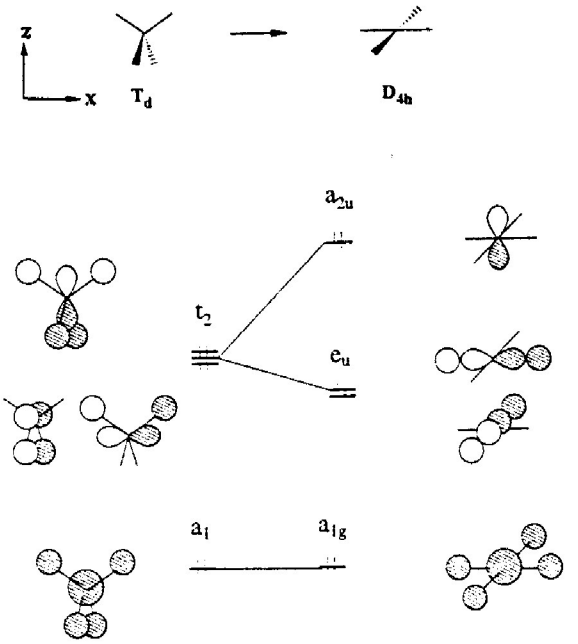
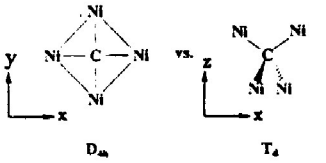


Fig. 4. Schematic orbital correlation diagram for the occupied molecular orbitals of CH_4 in T_d (left) and D_{4h} (right) geometries.

planar counterpart. The origin of the stability difference may be seen for CH_4 in Fig. 4. In a tetrahedral geometry, the t_2 orbitals form three C-H σ bonds, while in the square-planar conformation, the t_2 orbitals split into a bonding e_u set of orbitals and a high-lying a_{2u} orbital.

The latter is non-bonding, while the strength of the C-H bonding in the e_u orbitals of the D_{4h} geometry is almost a third smaller than that in the t_2 orbitals in the T_d geometry (as measured by computed overlap populations). The result is a net loss of C-H bonding in the planar geometry as compared to the tetrahedral one. We decided to look at a tetrahedral alternative for the $(Ni_4C)^{4-}$ molecular cluster, to see whether there was any factor discriminating against it. On going from a square planar $(Ni_4C)^{4-}$ model to a tetrahedral one (**5**, keeping Ni-C bond lengths constant: the computational details are not shown here), the three highest occupied orbitals in Fig. 1 become a totally bonding t_2 set. The Ni-C bonds are strengthened in the tetrahedral geometry of Ni_4C^{4-}, just as they are in the case of CH_4. Tetrahedral Ni_4C^{4-} is computed as 1.15 eV more stable than the D_{4h} form. There appears to be nothing wrong with this structure, though one loses some Ni-Ni bonding in departing from the square planar structure.



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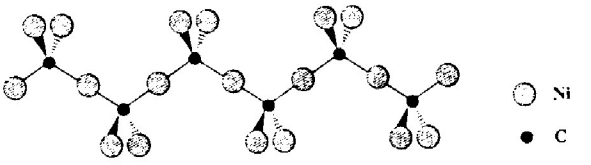
A similar situation should also arise in the extended structure. Using the tetrahedral building block shown at the right of **5**, we can construct a one-dimensional extended structure **6** (one of many possibilities). In hypothetical structure **6**, we keep the Ni-C bond lengths the same as in **2**. The resulting Ni-Ni separation is 3.04 Å.



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How do the energetics of the tetrahedral alternative compare to those of the planar geometry in the extended systems? The unit cell of **6** is $[Ni_6C_2]^{8-}$, containing twice as many atoms as in **2**. The extended Hückel calculation indicates that hypothet-

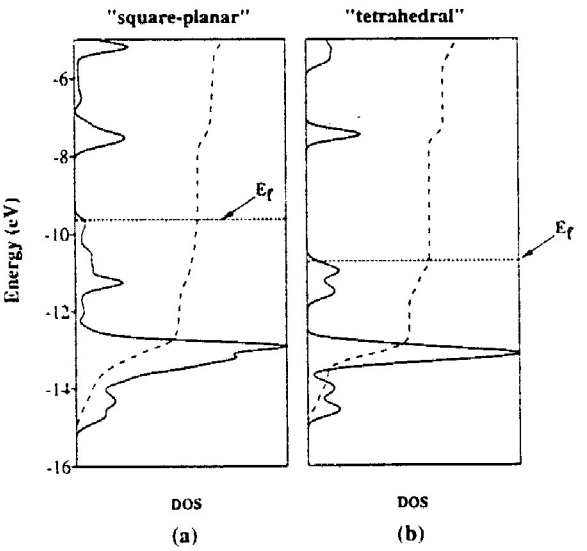


Fig. 5. Total DOS plots of (a) the "square-planar" structure (**2**) and (b) the "tetrahedral" one (**6**). The horizontal dotted line denotes the Fermi level.

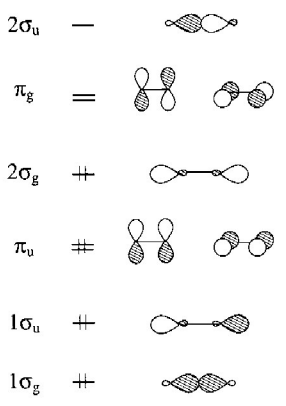
ical tetrahedral structure **6** is 1.24 eV more stable (per $[Ni_3C]^{4-}$ unit) than the structure cut out of the solid **2**. The total DOS of the tetrahedral chain **6**, is shown in Fig. 5 along with that of **2**. Compared to **2**, the Fermi level of **6** is lower in energy by 1.08 eV. The band gap at the Fermi level is 1.88 eV for **2** and 3.19 eV for **6**.

These findings are consistent in indicating greater stability for the tetrahedral alternative, despite diminished Ni-Ni bonding. (The Ni-Ni overlap population in **6** is –0.004, thus essentially zero.) We expect substantial stabilization for both alternatives upon adding on the C_2^{2-} groups, as we do in the next section.

4. Adding in the Terminal C_2 Units

One of the strategies devised for stabilizing square-planar carbon is to add σ-electron withdrawing groups [34 - 38]. Could that be a factor in our case? We add the C_2^{2-} ligands and study their influence on the electronic structure of $^1_\infty[Ni_3C_5]^{8-}$. In the actual structure the carbide units are bent about 10° from the Ni_4C plane, the carbides on one side of the $^1_\infty[Ni_3C]^{4-}$ chain going up in the z direction and those on the other side going down. In our calculations we have kept the carbides coplanar with the Ni_4C plane; calculations with bent carbides show negligible differences.

The orbitals of a C_2^{2-} group, isoelectronic with N_2, are well known and are shown in **7**.



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The short C-C bond length observed (1.21 Å) hints that the C-C bonding in these ligands is likely to resemble that of acetylene. The implication of this structural feature is that the "back-donation" of

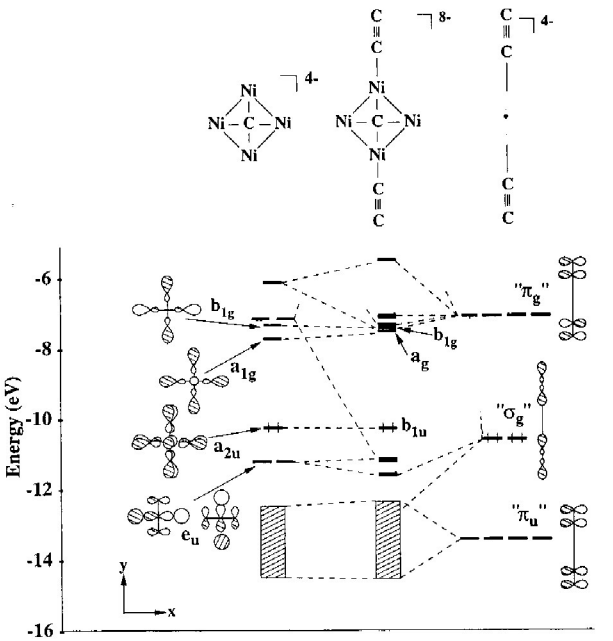


Fig. 6. FMO diagram of the model $(Ni_4C(C_2)_2)^{8-}$. For the C_2^{2-} ligands only one, representative orbital each is shown of π_u, σ_g, and π_g.

electrons from Ni atoms to the π^* orbitals (π_g) of the C_2^{2-} group is unlikely to be great. On the other hand, the Ni-C_2 (hereafter C_2 refers to the carbide group) bond length (1.87 Å) is shorter than a normal Ni-C single bond, which is around 1.90-2.05 Å[44]. Thus some degree of Ni-C π bonding is experimentally indicated.

This is supported by our calculations. Fig. 6 shows the fragment molecular orbital (FMO) diagram of the molecular model, $[Ni_4C(C_2)_2]^{8-}$ (of D_{2h} symmetry).

We have here typical organometallic bonding, with donation from the C_2^{2-} σ_g and some acceptance into acetylide C_2^{2-}. The b_{1u} orbital (the HOMO, related to the previously discussed a_{2u} of a square-planar geometry) of the molecular model is essentially unchanged upon addition of the terminal C_2^{2-} ligands.

In the polymer (whose band structure is not shown here) the two low-lying unoccupied bands that we saw above the Fermi level for **2** in Fig. 2 are pushed up. Except for an additional low-lying, unfilled band, the electronic structure resembles that of the $^1_\infty[Ni_3C]^{4-}$ polymer.

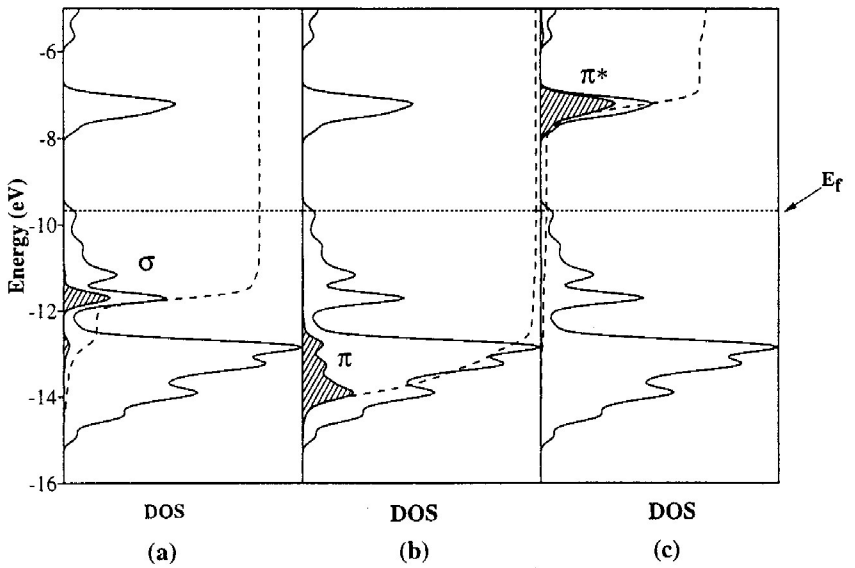


Fig. 7. DOS projections (shaded areas) for (a) the C_2^{2-} π_u orbitals, (b) the C_2^{2-} σ_u orbital, and (c) the C_2^{2-} π_g orbitals. The horizontal dotted line denotes the Fermi level, and the dotted curves are the integration of the projected DOS.

The overall interaction between the C_2^{2-} fragments and the core $^1_\infty[Ni_3C]^{4-}$ chain can be seen more clearly by looking at the contributions of C_2 orbitals to the total DOS plot, as presented in Fig. 7.

These projections show that the C_2 π_u (bonding) orbitals are mainly located in a band around –12.5 eV where they interact with the Ni p-d hybrid orbitals. The C_2 π_g (π^*) antibonding orbitals are in the bands around –7 eV. The integration of the π_g DOS (the dotted line in Fig. 7c) shows an almost imperceptible density of states below the Fermi level, indicating negligible Ni-C π interactions, i. e. little back-donation. This is consistent with the relatively unperturbed acetylenic C-C bond length. The overlap population of the C-C bond in **1** is calculated to be 1.91, compared to 1.88 in an isolated C_2^{2-} molecule and 1.93 in an acetylene (all C-C bond lengths are set for comparison to be 1.21 Å as in **1**).

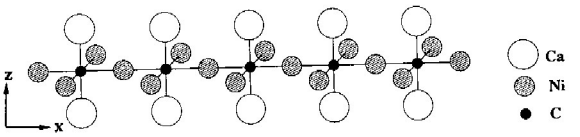
The effect of the terminal C_2^{2-} group on the core $^1_\infty[Ni_3C]^{4-}$ structure is also small, as judged by a Mulliken population analysis for **1** and **2**. The only significant change is net donation in the σ system, from C_2^{2-} to Ni.

5. Adding Ca to the model

We have found that neither the $^1_\infty[Ni_3C]^{4-}$ nor the $^1_\infty[Ni_3C_5]^{8-}$ sublattices give us a clue as to the stabilization of the square-planar geometry. The other ingredient in the original compound which we have not considered yet is the calcium framework around these infinite, one-dimensional C-Ni chains. If there were significant interaction (or bonding, or charge transfer) between the Ni-C anionic substructure and the Ca cationic framework, then removal of electrons from the Ni-C substructure might depopulate the problematic a_{2u} (Cp_z lone pair)-derived orbital. This by itself might stabilize the square-planar structure.

Still another viewpoint uses the isolobal analogy [45] to relate $d^{10}s^0p^0$ Ni^0 to s^0p^0 H^+, and CNi_4^{4-} to CH_4. Then an electron depleted CNi_4^{3-} might be analogous to CH_4^+ (which, according to calculation [46], prefers a near-planar over a tetrahedral geometry). CNi_4^{2-}, still more oxidized than our model system, is isolobal to CH_4^{2+}. This molecule has an empty a_{2u} orbital in the D_{4h} geometry, and thus prefers that geometry to tetrahedral in our calculations.

There are two types of Ca atoms in the observed crystal structure. The first kind is found above and below the Ni_4C plane, completing a rough octahedron around the tetracoordinate carbon. The second type is located above and below the space between the carbide end groups of neighboring $^1_\infty[Ni_3C_5]^{8-}$ chains. The first type of calcium is of special interest to us, both because of its short Ca-C contact (2.56 Å; the sum of the covalent radii is 2.50 Å [47]) and because of its location directly above the central C in the direction of the problematic "lone pair" of the a_{2u}-based orbital (see **8**). We



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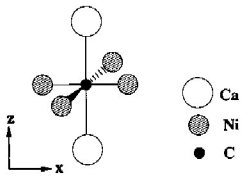
proceeded to carry out a series of model calculations with Ca ions.

Parameter choices for alkali metals and alkaline earths in the extended Hückel method are fraught with difficulty. If one uses parameters derived for neutral atoms, the ns and np orbitals come out high in energy and very diffuse. The result is little interaction. At the other extreme, parameters for group I or II metal ions (M^+, M^{2+}) give orbitals that are too low in energy and contracted. The outcome then is too much interaction. In an all-electron calculation with a large basis set this problem would be solved (or so one would like to think) by internal self-consistency; the normal extended Hückel parameters cannot accomodate to this. We looked for a parameter set giving some interaction, but not an excessive amount, and after some experimentation came up with that indicated in the Appendix.

If we go back to Ni_4C^{4-} (the first, slightly idealized, building block we have used to construct the polymer) and add the Ca^{2+}'s, we find that the new molecular unit, neutral Ca_2CNi_4 (**9**), is stabilized by 2.56 eV relative to **3**.

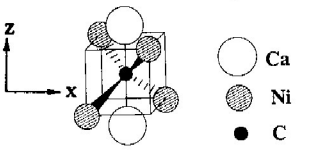


9

The new, pseudo-octahedral geometry about C lowers the HOMO by 0.52 eV through interactions between the C p_z and the out-of-phase combination of s orbitals on the Ca. The filled e_u set is also lowered through π interaction with the Ca p orbitals. This Ca-C mixing is accompanied by a charge transfer of about 0.5 electrons from C to Ca, and 0.1 electrons from each Ni to the Ca's.

The Ca_2Ni_4C units can be linked together into a chain, as they are found in the crystal structure of $Ca_4Ni_3C_5$. The resulting chain, $^1_\infty[Ca_2Ni_3C]$ (**8**), is 2.97 eV per formula unit more stable than the core $^1_\infty[Ni_3C]^{4-}$ polymer. As with the molecular model described above, the lowering in energy of the highest occupied band (through mixing of the C p_z and the Ca s orbitals) is an important factor in the stabilization of the entire chain, accounting for about 30% of the change. About 0.8 electrons are transferred from C to Ca, about 0.15 electrons from each edge Ni to Ca, and about 0.4 electrons from the bridging Ni to Ca. As with **9**, most of the charge is transferred to the s orbital on Ca, with some transfer to the p orbitals from the Ni's.

Adding Ca to the model clearly helps to stabilize the central carbon of the square-planar moiety by placing an electron-withdrawing group in spatial proximity to the lone pair on that carbon. However, we should consider this stabilization in reference to a possible pseudo-tetrahedral structural alternative. If we position the tetrahedron formed by the four Ni's around $C_{central}$ inside an imaginary cube such that the Ni's lie at vertices of the cube, we can place Ca's along axes running from the center of the cube (the C) through opposite cube faces. This geometry, which could be called an edge-bicapped tetrahedron, keeps the Ca-C-Ca bond linear and minimizes crowding between Ca and Ni, as shown in **10**. An alternative choice — "face-capping" Ca's at two of the four open cube vertices — puts the Ca's further from the nickels but does not keep Ca-C-Ca at 180°.



10

This unit turns out to be 2.04 eV more stable than the pseudo-octahedral model! **10** is 3.45 eV more stable than the tetrahedral unit without Ca. As in the case of CH_4 (but less obviously), the change in C coordination geometry enables increased Ni-C p orbital overlap, and in that way stabilizes the a_{2u} orbital, the HOMO of the system. This stabilization accounts for two thirds of the stabilization of the entire complex.

We can link these "tetrahedral" units into a chain as we did with **9**. The resulting chain **11** has a doubled unit cell, $Ca_4Ni_6C_2$. It is easy to visualize the "squashing" distortion at each C that would transform **11** into **8**.

11 is 1.76 eV more stable than **8**; 50% of this stabilization comes from the stabilization of the a_{2u}-based, highest occupied band.

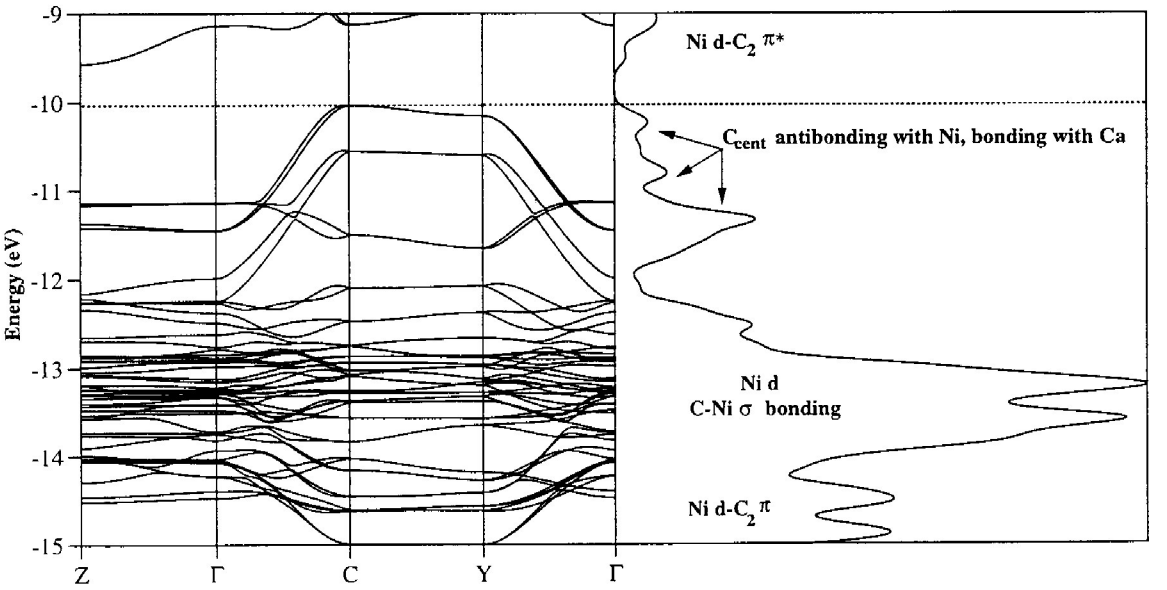
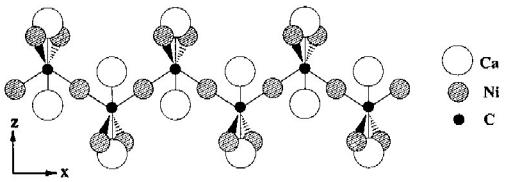


Fig. 8. Band structure and DOS plot of $Ca_4Ni_3C_5$. On the right, the principal DOS peaks are labeled with the main bonding encountered in the corresponding bands.



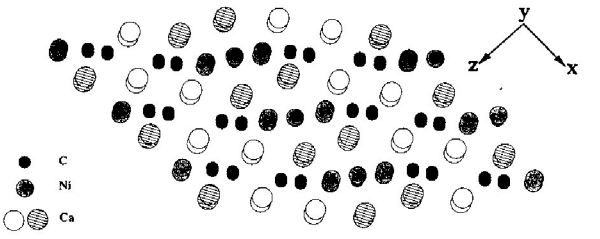
11

Adding the terminal carbides to **8**, **9**, **10** and **11** lowers their total energy, but the isolated tetrahedral systems are still lower in energy than their square-planar counterparts. So while the Ca coordination described above helps to stabilize the square-planar arrangement of Ni around C, this stabilization is apparently still insufficient to favor a square-planar C coordination over a tetrahedral one.

6. The Full Complex

It would have been nice if the factors stabilizing the square planar geometry had emerged in any of the sublattices studied. But this was not to be (unless the extended Hückel method is at fault here, which is certainly possible). We are left to find the stabilization in the remaining Ca ions in the structure, those that stitch together the entire three-dimensional network. Let's see if we can gain some insight into what is going on.

The $^1_\infty[Ni_3C_5]^{8-}$ chains are held together not only by the Ca ions axial to the central carbide (large lined circles in **12**), but also by other Ca ions located between the carbide groups of neighboring chains (large white circles in **12**). These other Ca ions are near the acetylide units of several different organometallic chains. The "axial" calciums (lined circles) also come near C_2 units of a neighboring chain.



12

We have made some effort to think of alternative structures in which "tetrahedral" chains (along the lines of **11**) are held together by Ca^{2+} ions, but we have not come up with any that give an efficient, dense crystal packing. It must be said right away that our search was not systematic. And it is a non-trivial task to predict the three-dimensional structure of a molecule [48].

In the end we have failed to find a completely satisfying, simple orbital reason for the stabilization of the square planar $Ni_3C_5^{8-}$ chain in $Ca_4Ni_3C_5$. The axial calcium atoms are important, but they are not the whole story.

We can calculate the electronic structure of the full $Ca_4Ni_3C_5$ lattice **12**. The band structure and DOS of the $Ca_4Ni_3C_5$ structure are shown in Fig. 8.

Major features in the DOS curve are identified according to the bonding occuring in the corresponding bands. The DOS is very similar to that of the $^1_\infty[Ni_3C_5]^{8-}$ chains (see Fig. 7). The Ca's carry a charge of +1.25 on average, indicating about one third population of the Ca orbitals. A projection of the Ca contributions to the DOS (not shown here) shows small contributions throughout the filled states, with a more significant density from the Ca near $C_{central}$ in the peaks between −12 and −10 eV. The structure should be semiconducting, possessing as it does a reasonable band gap.

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Table I. Parameters used in the extended Hückel calculations.

Atom	Orbital	H_{ii}	ζ_1	c_1 [a]	ζ_2	c_2 [a]	References
C	2s	−21.40	1.625				[30]
	2p	−11.40	1.625				
Ni	4s	−9.21	2.00				[40, 52]
	4p	−5.29	2.00				
	3d	−13.18	5.55	0.5679	2.10	0.6059	
Ca	4s	−9.00	1.20				
	4p	−6.60	1.20				

[a] Coefficients in double-ζ expansion.

Appendix

Computational details

The calculations presented in this work are in the framework of the extended Hückel [25, 26, 30, 49] tight-binding method [28, 29, 31], and utilized the YAeHMOP package [50]. The parameters used in our calculations are listed in Table I, and the off-diagonal elements of the Hamiltonian were evaluated with the modified Wolfsberg-Helmholtz formula [51]. Numerical integrations over the symmetry-unique section of the Brillouin zone of the one-dimensional structure were performed using a set of 100 k-points. The three-dimensional structure calculations used 84 k-points.

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