

## Planar Tetracoordinate Carbon in Extended Systems

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**Abstract:** A recently proposed system with a central planar tetracoordinate carbon linking two three-membered rings,  $C_5^{2-}$ , lends itself to extension in one, two, and three dimensions. Our construction of potential realizations begins with an analysis of the electronic structure of  $C_5^{2-}$ . Dimers such as  $C_{10}Li_3^-$ ,  $C_{10}Li_4$ , and a trimer  $C_{15}Li_6$  are then examined, and their geometries are optimized to find clues for ways the  $C_5^{2-}$  unit may polymerize in the presence of countercations. Coordination through the terminal carbons is favored in the oligomers and polymers; several electronically and structurally reasonable systems of the stoichiometry  $C_5M_x$  ( $M = Li$ ,  $x = 2$ ;  $M = Be, Pt, Zn$ ,  $x = 1$ ) emerge from band structure calculations and energetic considerations.

## Introduction

Stabilization of planar tetracoordinate carbon ( $C_{pt}$ ) continues to be a fascinating experimental and theoretical challenge.<sup>1–11</sup> For a  $C_{pt}$  surrounded by four other carbons, the simplest molecule that (so far on paper, or rather in silico) achieves this goal is  $C_5^{2-}$ .<sup>12</sup> Its metastability is a consequence of the delocalization of the electrons in the p orbital of the central carbon.<sup>13</sup> The possibility of an extended network based on motifs containing a  $C_{pt}$  surrounded by other elements has been explored previously.<sup>14–16</sup> The  $C_5^{2-}$  system appears to be a good starting point for exploring polymeric forms containing  $C_{pt}$ , which is the focus of this paper.

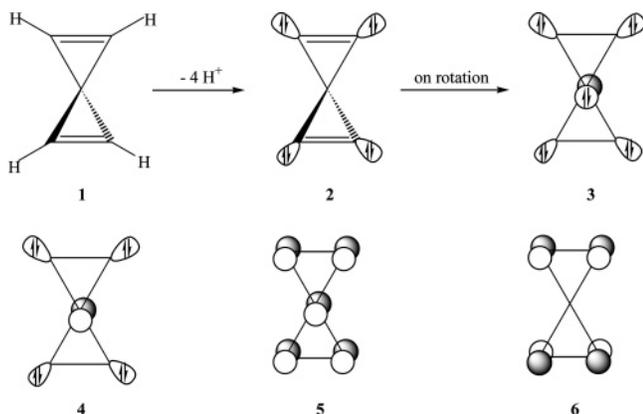
## Computational Methodology

The geometry optimizations of the discrete molecular systems ( $C_5Li_2$ ,  $C_5Li_4^{2+}$ ,  $C_{10}Li_3^-$ ,  $C_{10}Li_4$ ,  $C_{15}Li_6$ ) reported in this paper are performed using Gaussian 98.<sup>17</sup> Structures are optimized using Becke's exchange (B), Lee, Yang, and Parr (LYP) correlation, and the hybrid functional (B3LYP) approach,<sup>18,19</sup> as implemented in the Gaussian set of programs. All the molecular calculations are done with the 6-311++G(2d) basis set.<sup>20</sup> Calculations have been performed on various extended networks of  $C_5M_x$  ( $M = Li$ ,  $x = 2$ ;  $M = Pt, Zn, Be$ ,  $x = 1$ ) using the extended Hückel (EH) based YAeHMOP program to verify the stoichiometry.<sup>21</sup> A special case of  $C_5Zn$  where Zn and the  $C_{pt}$  are interchanged in positions is also considered. For geometry optimization of the extended models, the density functional theory (DFT) based VASP program is used.<sup>22–25</sup> The ultrasoft pseudopotentials employed in VASP are based on the projector-augmented-wave (PAW) method.<sup>26</sup> The Perdew–Wang 91 (PW91) functional within the generalized

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**Figure 1.** Simplified picture of the construction of the MOs (4, 5, 6) of  $C_5^{2-}$  from  $C_5^{4-}$  (2) derived from  $C_5H_4$  (1). 3 is the intermediate  $C_5^{4-}$  in a planar geometry.

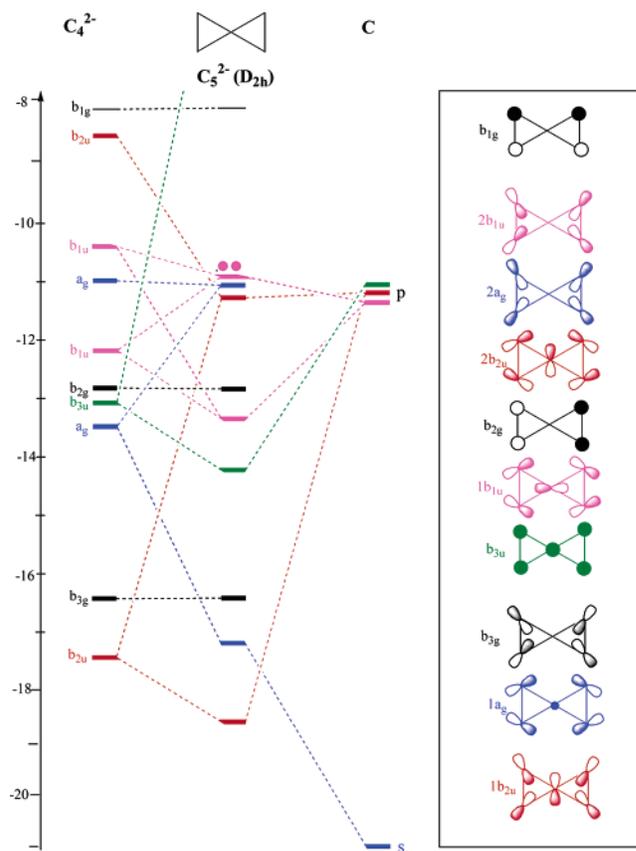
gradient approximation (GGA) is used to treat the exchange-correlation energy.<sup>27–29</sup> A cutoff energy of 500 eV and an energy convergence of  $1.0e-07$  eV  $\text{atom}^{-1}$  are used. For the crystal lattice, integration over the symmetrized Brillouin Zone is performed using the k-points generated via the Monkhorst–Pack scheme.<sup>30</sup> In all systems, the generation of the mesh a uniform k-point separation of  $2 \text{ pm}^{-1}$  is employed. The geometry is well converged with respect to the plane-wave energy cutoff and k-point sampling.

### Why $C_5^{2-}$ ?

One way to describe simply the MOs of  $C_5^{2-}$  and why it features a  $C_{pt}$  is to start with a spiropentadiene, **1** (Figure 1). Four protons can be formally removed from  $C_5H_4$ , **1**, to obtain  $C_5^{4-}$ , **2**. This generates four lone pairs, one on each terminal carbon ( $C_t$ ) and pointing outward, roughly in the direction where the hydrogen nuclei were located in **1**. Rotating one cyclopropenyl ring against the other, to put all five carbons into one plane, results in planar  $C_5^{4-}$ , **3**. The central  $\pi$ -type lone pair, a characteristic feature of square planar carbon systems, will be surely destabilized. Vacating this MO will result in  $C_5^{2-}$ , **4**, for which there are four out-pointing lone pairs and a  $\pi$ -system of two occupied orbitals, which must be **5** and **6** (schematic).

In a second approach, Figure 2 constructs the molecular orbitals (MOs) of  $C_5^{2-}$  from the interaction of four  $C_t$ 's with the central  $C_{pt}$ . The energy level positions come from an extended Hückel (EH) calculation<sup>31</sup> on a DFT-optimized geometry of the  $C_5^{2-}$  molecule. The colors distinguish the MO symmetries. Those MOs which contain no contribution from the  $C_{pt}$  by symmetry are assigned black. The  $\sigma$  MOs emphasize the radial and tangential p orbital origins.

The four localized lone pairs of **4** (Figure 1) should transform as  $a_g + b_{1u} + b_{2u} + b_{3g}$ . Their delocalized equivalents are to be found in  $1b_{2u}$ ,  $b_{3g}$ ,  $2a_g$ , and  $2b_{1u}$  of Figure 2. Two very low-lying MOs ( $a_g$  and  $b_{1u}$ ) with mainly s character are omitted in the diagram. The destabilization of  $2a_g$  and  $2b_{1u}$  (mostly bonding) over  $1b_{2u}$  and  $b_{3g}$  (mostly antibonding) is due to the second-order interaction with the  $\sigma$  set of MOs. Since these radial MOs mix with the tangential MOs ( $1a_g$ ,  $1b_{1u}$ , and



**Figure 2.** Correlation diagram between the four  $C_t$  and the central  $C_{pt}$  generating the MOs of  $C_5^{2-}$ . The bold and thin lines differentiate between the filled and empty levels.

$2b_{2u}$ ) due to their common symmetry, the orientation of the canonical orbitals differs slightly from those shown schematically in Figure 2. The  $p$  orbitals perpendicular to the plane, which are involved in the formation of  $\pi$  MOs, are shown as circles, symbolizing their “top” (above the plane) phase. The two  $\pi$  MOs **5** and **6** (Figure 1) are identified as  $b_{3u}$  and  $b_{2g}$  in Figure 2. The corresponding antibonding combination lies even above the LUMO ( $b_{1g}$ ).

### Discrete systems

Counteranions are used to further stabilize the system ( $C_5^{2-}$ ). Calculations on  $C_5^{2-}$  using two  $Li^+$  ions to balance the charge result in three different isomers of  $C_5Li_2$  (**7–9**, Figure 3) distinguished by the position of Li ions. The calculated energies of **7–9** indicate that the metal ions prefer coordinating the carbons not linked to each other.

To understand the arrangement of four  $Li^+$  ions around a  $C_5^{2-}$  unit, two isomers were explored (**10** and **11**, Figure 3). In this case, isomer **10** is found to be more stable than **11** by  $51.4 \text{ kJ mol}^{-1}$ . **10** maximizes the electrostatic interactions between the lone pairs at the four  $C_5^{2-}$  corners and the four  $Li^+$  ions and is the one dictated by two of the three highest lying occupied MOs ( $2b_{1u}$  and  $2a_g$ ) of  $C_5^{2-}$  (see Figure 2).

The design of a fragment containing two  $C_5^{2-}$  units (a dimer) would require including four monocations ( $Li^+$ ) in order to keep the electroneutrality of the system. The relative stabilities of the monomers give an idea of how to arrange the metal ions around the  $C_5$  unit. The most stable isomer in the  $C_5Li_2$  series calculated here<sup>32</sup> (**7**) suggests two possible arrangements for a

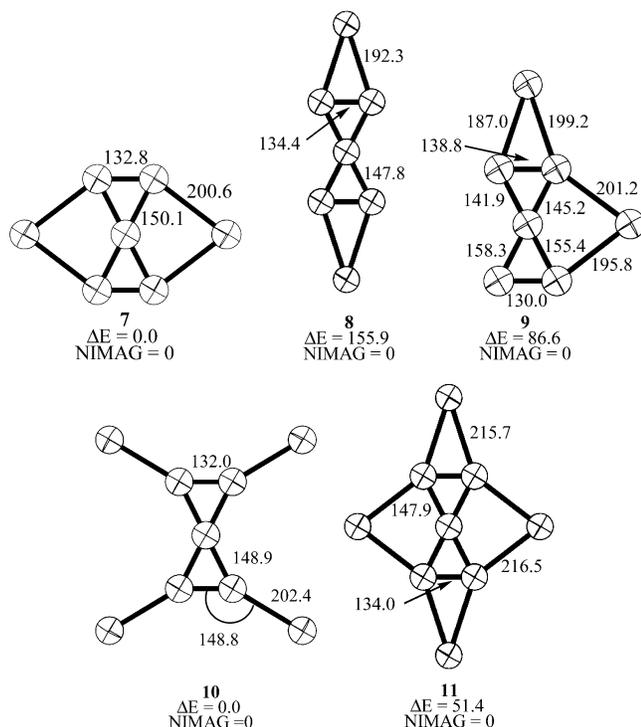
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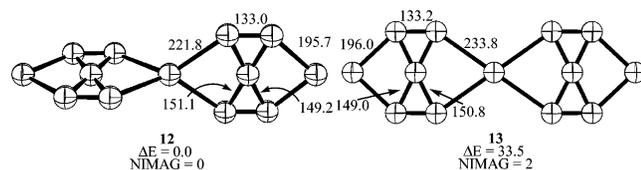
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**Figure 3.** Possible isomers (7–9) of  $C_5Li_2^+$  and (10 and 11) of  $C_5Li_4^{2+}$  with varying metal positions are shown.  $\Delta E$  is the relative energy (in  $\text{kJ mol}^{-1}$ ) with respect to the most stable isomers 7 and 10 of  $C_5Li_2^+$  and  $C_5Li_4^{2+}$ , respectively. All these structures are local minima on the PES as observed from the number of imaginary frequencies (NIMAG).



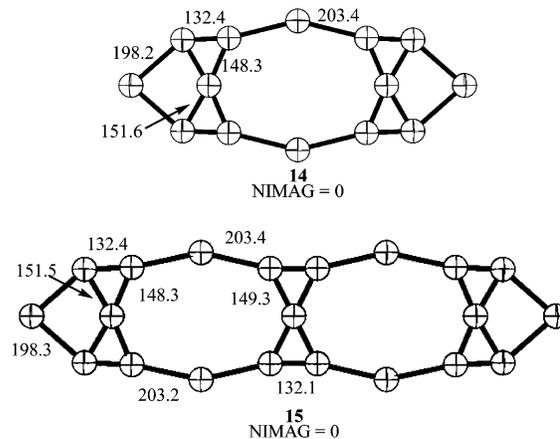
**Figure 4.** Two possible isomers (12 and 13) of  $C_{10}Li_3^-$  with perpendicular and coplanar  $C_5^{2-}$  units.  $\Delta E$  is the relative energy (in  $\text{kJ mol}^{-1}$ ) with respect to 12.

$C_{10}Li_3^-$  dimer; one where both  $C_5^{2-}$  units are perpendicular to each other, 12, and another, where the units are coplanar, 13 (Figure 4). Structure 12 is a minimum on the potential energy surface (PES), while 13 has two imaginary frequencies.

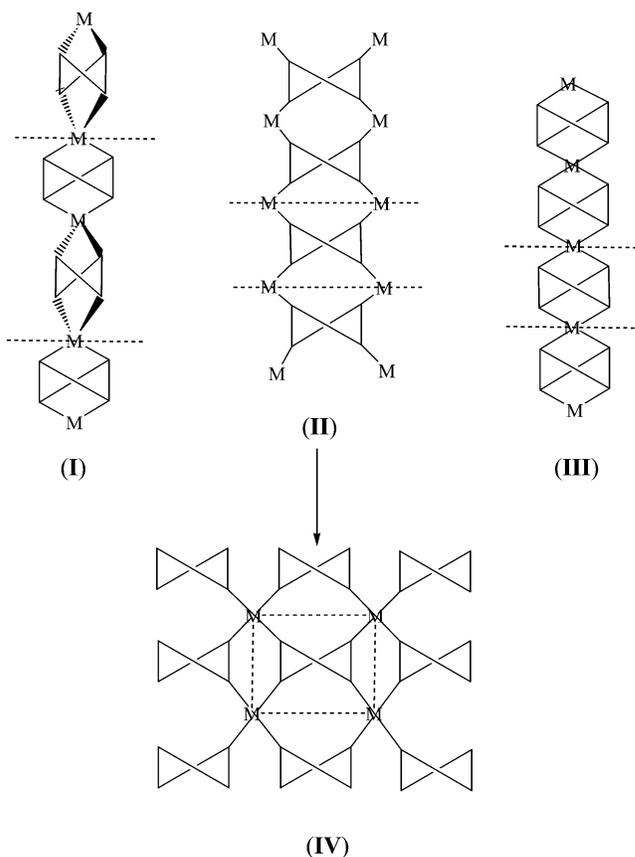
The most stable structure 10 in the  $C_5Li_4^{2+}$  series leads to a dimer  $C_{10}Li_4$  (14, Figure 5). In the optimized structure, two of the  $Li^+$  ions occupy positions between the terminal carbons which are not linked to each other. To gain further insight on the preferred position of the metal, a trimer  $C_{15}Li_6^{2-}$  15 (Figure 5) is also constructed; it continues the bonding motif found for 10. Both 14 and 15 are minima on their PES. These results provide clues for extending the system in two and three dimensions.

### Extended Networks based on $C_5^{2-}$

Based on the results in the previous section, different 1-D and 2-D networks can be constructed. The stable dimers 12 and 14, as well as structure 13, lend themselves to extension to 1-D chains of  $C_5$  units. These polymeric chains are depicted in Figure 6 as I, II, and III, respectively. Since the ratio of a  $C_5$  unit to



**Figure 5.** Optimized structures of  $C_{10}Li_4$  and  $C_{15}Li_6$ .



**Figure 6.** Schematic diagram for a 1-D (I, II, III) and a 2-D (IV) pattern of  $C_5^{2-}$  units bridged by appropriate metal ions.

the metal in a unit cell of I and III is 1:1, a divalent metal ion is needed to compensate for the 2- charge on  $C_5$ . II involves a 1:2 ratio of  $C_5$  to metal, which might be supported by  $Li^+$  ions. If  $Li^+$  is replaced by a divalent tetracoordinate metal ion, II can be converted into a 2-D network, as shown in IV, Figure 6. The repeating units are shown by dashed lines.

Since I involves a tetrahedral coordination around the metal and the requirement of a divalent metal ion, a  $Zn^{2+}$  or  $Be^{2+}$  ion can be chosen for building the network. The choice of Zn and Be is based on the existence of systems containing  $(Zn/Be)^{2+}$  with a tetrahedral arrangement, for e.g.,  $Zn(CN)_2$  and  $CBe_2$ .<sup>33,34</sup> In the case of II,  $Li^+$  ions are retained, as in structures 14 and 15, whereas, for III, platinum might be a good choice,

(32) There may be other more stable  $C_5Li_2$  isomers with a nonsquare-planar carbon (see ref 13).

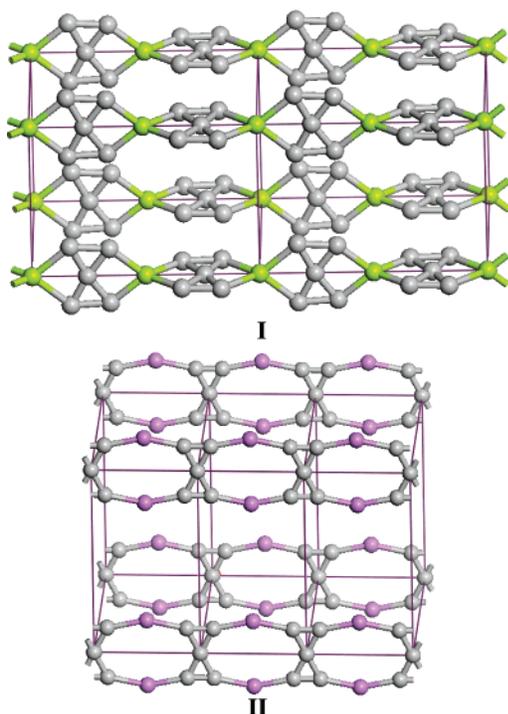


Figure 7. Optimized lattice of (I)  $C_5Zn$  and (II)  $C_5Li_2$ .

Table 1. Space Group, Z, Cell Parameters ( $a$ ,  $b$ ,  $c$  in Å), and  $V$  (Volume in Å<sup>3</sup>) of the Different  $C_5M_x$  Systems Are Given

system	space group	Z	$a$	$b$	$c$	$V$
$C_5Zn$ (I)	$P42/mmc$	2	9.90	9.90	9.33	915.14
$C_5Li_2$	$Pmmm$	1	5.33	9.91	9.97	526.80
$C_5Pt$	$Pmmm$	1	3.84	4.46	5.22	89.32
$C_5Zn$ (V)	$P42/mmc$	2	4.76	4.76	9.14	206.56
$C_5Be$	$P42/mmc$	2	4.45	4.45	8.82	174.83
$C_5Zn$ (VII)	$P42/mmc$	2	3.78	3.78	10.53	150.46
$C_5Ni$	$P42/mmc$	2	3.82	3.82	10.44	152.04

as it often exists in a square planar arrangement with an oxidation state of II.<sup>35</sup> The 2-D network of IV might be realized with Pt as metal ions as well. While the results from the studies on molecular systems showed two most preferred positions for metal ions, (i.e., either bonding the  $C_t$ s or connecting two  $C_t$ s which are not bonded to each other), the two polymorphic forms of  $C_5Pt$  (III and IV) will enable one to say which among these two provides the most stable site for the metal ions.

Phase I is found to be stable with Zn;  $C_5Be$  failed to converge.  $C_5Zn$  (I) and  $C_5Li_2$  (II) are optimized in a 3-D lattice, and the resulting geometries are shown in Figure 7.  $C_5Be$  (I) has a tetragonal unit cell (space group  $P42/mmc$ ), while II has an orthorhombic unit cell (space group  $Pmmm$ ).

The optimized lattice parameters of I are given in Table 1. Due to the difficulty VASP has in dealing with 1-D systems, a 3-D system is used with the discrete chains well separated from each other (as can be seen from the cell parameters of  $\sim 1000$  pm for  $a$  and  $b$  in Table 1). The large separation is retained even after convergence, which essentially implies that the system

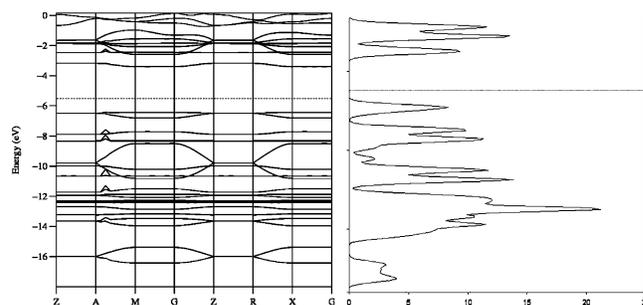


Figure 8. Band structure and total DOS for optimized  $C_5Zn$  (I).

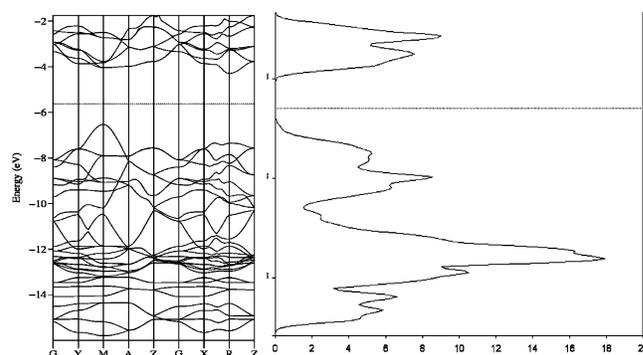


Figure 9. Band structure and total DOS of optimized  $C_5Li_2$ .

wants to remain one-dimensional. The DFT based band structure and total DOS for I are shown in Figure 8.

The C–C bond lengths within the  $C_5^{2-}$  unit of I closely resemble the values calculated for the corresponding dimer,  $C_{10}Li_3^-$  (12); the bond lengths range from 135 to 149 pm. In general the  $C_t$ – $C_t$  bonds tend to be shorter compared to the  $C_t$ – $C_{pt}$  bond in all the systems studied here. The extent of shortening of the  $C_t$ – $C_t$  bond can be correlated to the back-donation from  $C_{pt}$ . Thus the terminal  $C_t$ – $C_t$  bond (133 pm) which can be related to an acetylenic bond, is disturbed by partial back-donation from the central  $C_{pt}$  to one of the  $\pi^*$ -bonds (in-plane) of  $C_t$ – $C_t$ . The MOs which contain contributions from the in-plane  $\pi$  and  $\pi^*$ -MOs of  $C_t$ – $C_t$  emerge as the tangential MOs in  $C_5^{2-}$ ,  $1a_g$ ,  $1b_{1u}$ , and  $2b_{2u}$  as seen in Figure 2. Here  $2b_{2u}$ , which is antibonding between  $C_t$ , can be identified as involving back-donation from  $C_{pt}$  to the in-plane  $\pi^*$  of  $C_t$ – $C_t$  and contributes to some extent to the elongation of the  $C_t$ – $C_t$  bond. The Zn– $C_t$  and Zn– $C_{pt}$  distances are 212 and 233 pm, respectively.

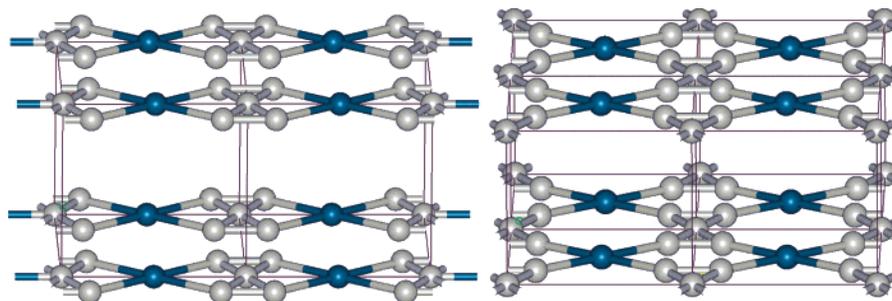
In  $C_5Li_2$ , the geometrical parameters are not very different from the calculated dimer (14) and trimer (15). The optimized unit cell dimensions are given in Table 1. The C–C bonding distance within the  $C_5$  unit ranges from 133 to 150 pm. In the optimized lattice, the discrete chains remain separated from each other by  $\sim 1000$  pm (see  $b$  and  $c$  values in Table 1). The calculated band structure and DOS obtained from VASP for  $C_5Li_2$  are shown in Figure 9; the band gap is  $\sim 3$  eV. The bands are almost flat, as the interactions with the Li atoms binding the  $C_5$  units are almost negligible.

$C_5Pt$  in a 3-D lattice is optimized in an orthorhombic unit cell, space group  $Pmmm$  (Figure 10). On geometry optimization, III actually went over to IV, proving that the metal prefers to stay entirely bonded to the  $C_t$  atoms of the  $C_5$  unit, one among the two possibilities found by calculations on the discrete systems. This is also reflected in the relative stabilities of the

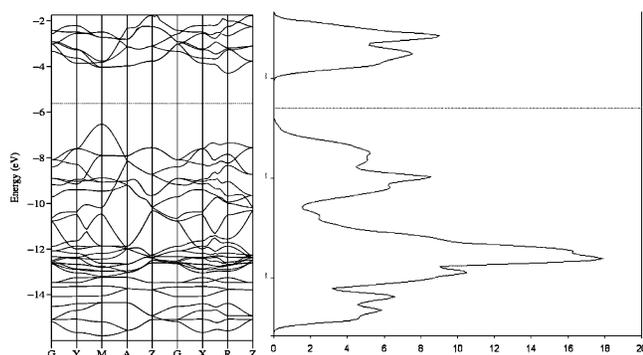
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**Figure 10.** 3-D unit cells of the **III** and **IV** forms of  $C_5Pt$  are shown. **III** correspond to the initial geometry and **IV** to the relaxed structure.



**Figure 11.** Calculated bands and total DOS of the optimized  $C_5Pt$  system.

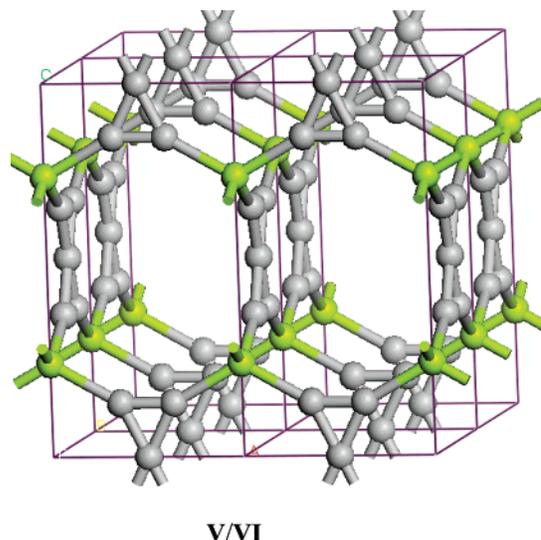
isomeric forms of  $C_5Li_4^{2+}$ , with **10** being more stable than **11** by 51.4 kJ mol<sup>-1</sup>. The transformation may be viewed as the migration of Pt from the edge (*b* axis) in **III** to the face in **IV**, along the *c* axis.

The optimized unit cell dimensions for **IV** are given in Table 1. The nonbonding distances between the  $C_t$  atoms of the neighboring units are 314 and 254 pm along the *b* and *c* axes, respectively. Hence, the  $C_5$  units are well-isolated from each other and are connected only through the bridging Pt ion. The C–C distances within the  $C_5$  unit reproduce the trend observed in its molecular analogues ( $C_t$ – $C_t$  132.0 pm,  $C_t$ – $C_{pt}$  149 pm). Though Pt maintains a planar arrangement, the ligands are not at the corners of a square; the calculated  $C_t$ –Pt– $C_t$  bond angles are 102° (*b* axis) and 78° (*c* axis), respectively.

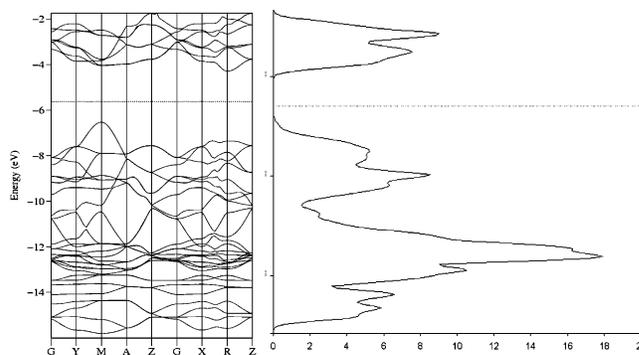
The band structure and the total density of states (DOS) for **IV** are given in Figure 11. A band gap of ~1 eV indicates semiconducting behavior.

Based on the above observation regarding the preferred position of metal ions, a 3-D network is designed with Zn/Be (**V**, **VI**) connecting the  $C_5$  units by bridging through the  $C_t$  atoms. Figure 12 gives the unit cell of  $C_5M$  ( $M = Zn, Be$ ); the  $C_5$  units run along the *a* and *b* axes, and the metal connecting them adopts a tetrahedral environment. The structure is tetragonal and belongs to space group  $P42/mmc$ . The essential parameters of the optimized system are given in Table 1.

The computed bond lengths of Zn–C and Be–C are in close agreement with the known systems (Zn– $C_2N_2$  = 192 pm and Zn– $C_5$  = 197 pm, Be<sub>2</sub>–C = 188 pm and Be– $C_5$  = 179 pm). The nonbonding  $C_t$ – $C_t$  distances, same along the *a* and *c* axes by symmetry, are 344 and 313 pm for Zn and Be systems, respectively. The geometry of the  $C_5$  unit does not deviate from the values calculated earlier, with normal  $C_t$ – $C_t$  [131.6 (Zn) and 132 (Be)] and  $C_t$ – $C_{pt}$  [147 (Zn) and 148 (Be)] distances. The angles around Zn and Be deviate from a perfect tetrahedron,



**Figure 12.** Unit cell of a 3-D network of  $C_5M$  ( $M = Zn, Be$ ).

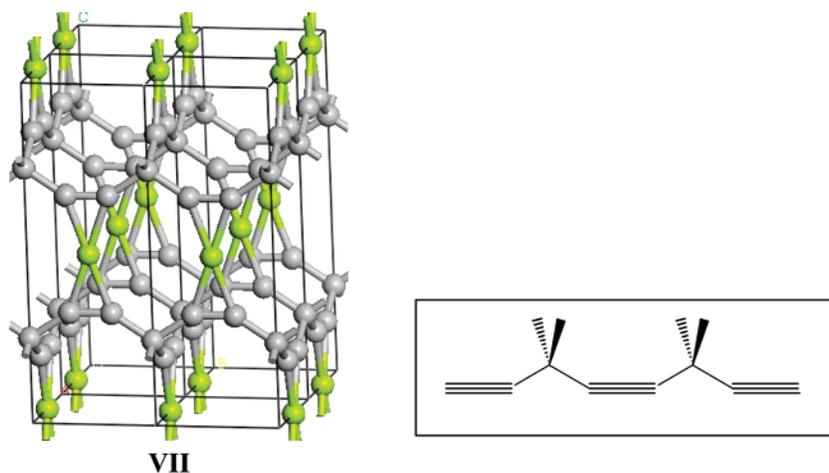


**Figure 13.** Calculated bands and total DOS of optimized  $C_5Zn$ .

with values of around 121° (between atoms along the same axes) and 104° (between two different axes).

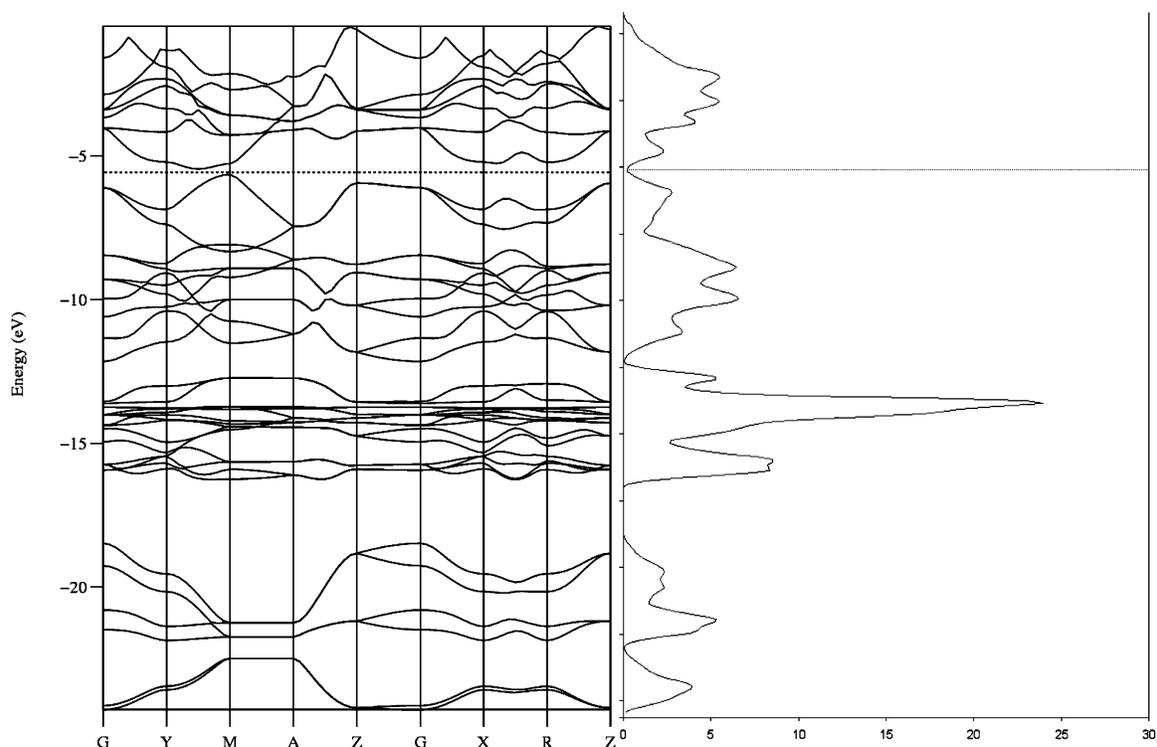
The band structure and total DOS for  $C_5Zn$  are given in Figure 13. This system and the analogous Be one (calculated, but details are not shown here) have a band gap of ~2–3 eV, indicating insulating behavior. The band structure of the Be phase (not shown in detail here) exhibits similar features especially near the Fermi level. The bands in the region of 11–14 eV in  $C_5Zn$  are the d-band of Zn. A detailed analysis, not shown in the figure, indicates a small participation of Zn 3d levels and slightly stronger bonding in Zn–C than Be–C.

$ZnC_5$  (**V**) is polymorphic to the already calculated system **I**. **V** is found to be more stable than **I** by 685 kJ mol<sup>-1</sup> per  $ZnC_5$ , further suggesting the greater preference of the metal ion to bond exclusively to the  $C_t$  atom of  $C_5^{2-}$  unit.



VII

**Figure 14.** Unit cell of  $C_5M$  (VII) with M at the square planar and C at the tetrahedral positions. The inset shows the skeleton of the carbon chain running along the  $a$  and  $b$  axes.



**Figure 15.** Bands and the total DOS of  $C_5Zn$  (VII).

### An Isomer of $C_5Zn$ without a $C_{pt}$

We have also explored an isomeric form of  $C_5M$  (VII) ( $M = Zn, Ni$ ) with the tetrahedral and square planar atom identities interchanged relative to Figure 12 (Figure 14). Though square planar coordination around Zn is a rarity, there have been a few reports of these in the literature.<sup>36</sup> The resulting  $P42/mmc$  network has optimized lattice parameters given in Table 1. The  $a$  and  $b$  axes are considerably compressed owing to the shortening of the  $C_1-C_1$  bond to 129 pm (Table 1). The carbon skeletal pattern in this structure is entirely different; one way to think of the network is as an acetylenic complex of M (Figure 14). The  $C_1-C_1$  bond is much shorter compared to that of V, which shows the  $\pi$ -back-donation is not very strong with Zn. This is probably due to the very large differences in the orbital energies of Zn and C.

A comparison of the energies between the two forms of  $C_5Zn$  (V and VII) shows the latter (C in tetrahedral sites) to be more stable than the former one (Zn in tetrahedral sites) by an energy of  $122 \text{ kJ mol}^{-1}$  per  $C_5Zn$  unit. The band structure and total DOS of VII is given in Figure 15. The very small Fermi gap indicates that this structure is likely to be a semiconductor. The band structure of  $C_5Ni$  showed metallic behavior but a larger band gap compared to  $C_5Zn$  at an electron occupation appropriate to Zn. The EH calculation on the C sublattice alone also gave a definite band gap. This supports the perception of the carbon skeleton in this structure (see drawing in inset of Figure 14) being well described by a classical Lewis structure; hence Zn probably exists here in a zero oxidation state.

(36) Brock, S. L.; Kauzlarich, S. M. *Inorg. Chem.* **1994**, *33*, 2491.

## Conclusions

$C_5^{2-}$  is an interesting building block for potentially realizable 3D networks with  $C_{pt}$ , both with main group and transition elements. This paper is the first report on the theoretical design and hypothetical characterization of such a stable network. Theoretical studies on discrete systems containing  $C_5^{2-}$  units show two preferences in counteraction coordination: (a) through the outer carbon lone pairs of the  $C_5^{2-}$  unit and (b) through the terminal carbons, but with the metal binding the two nonbonded  $C_1$  atoms. Among the two, the former is preferred in monomers based on the relative stabilities of the isomeric forms studied. We construct a variety of extended networks derived conceptually from the monomer and dimer models and using a simple model of the bonding capabilities of the  $C_5^{2-}$  unit. The hypothetical  $C_5M_x$  ( $x = 1$ ,  $M = Pt, Zn, Be$ ;  $x = 2$ ,  $M = Li$ )

systems proposed in this work in general have relatively large band gaps, suggesting semiconducting or insulating behavior.

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**Supporting Information Available:** The computed energies, symmetries, and coordinates for all the reported systems, both molecular and extended. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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