Tetracoordinate planar carbon (TPC) has attracted considerable attention since it was first proposed by Hoffmann et al.\(^1\) thirty years ago. Designing new forms of TPC-containing systems and revealing the bonding nature of carbon beyond the conventional tetrahedral concept remain an important topic in both theory and application. Recent photoelectron spectroscopic measurements and ab initio theoretical investigations confirmed the existence of TPC in pentaatomic measurements and ab initio theoretical investigations confirmed conventional tetrahedral concept remain an important topic in systems and revealing the bonding nature of carbon beyond the able attention since it was first proposed by Hoffmann et al.\(^1\) 

**Chemical Structures**

![Chemical Structures](https://i.imgur.com/3H3G5.png)

Geometrical optimizations and electronic structural analyses of the \(-\text{O}_2\text{B}_3\)− bridged hydrometal complexes \((\text{M}_4\text{H}_3\text{X})_2\text{B}_2\text{O}_2\) and \((\text{M}_4\text{H}_3\text{N})_2\text{B}_2\text{O}_2^{2−}\) (\(\text{M} = \text{Ni, Mg}\)) containing double tetracoordinate planar nonmetals (TPN) have been performed using the density functional theory at the B3LYP/6-311+G(d,p) level. Theoretical evidence of the possibility of double TPN centers coexisting in one planar molecule is presented.

As can be seen from Figure 1, B atoms, which replace an H in each \(\text{Ni}_3\text{H}_4\)X and link the two building units through the rhombus \(-\text{B}_2\text{O}_2\)−, play a central role in maintaining the planarity of both \(\text{C}_1\) (\(\text{Ni}_4\text{H}_3\text{N})_2\text{B}_2\text{O}_2^{2+}\)) and \((\text{Ni}_4\text{H}_3\text{C})_2\text{B}_2\text{O}_2\). B utilizes one of its three \(sp^2\) hybrids to form a two-electron three-center bond with two neighboring Ni atoms whereas the other two hybrids participate in the formation of the two \(\text{B}−\text{O}\) bonds in the \(\text{B}_2\text{O}_2\) bridge. Maintaining the eight \(2e\)−\(3c\) bonds along the peripheries of the two Ni rings is confirmed to be important in stabilizing these complexes, as in the cases of \(X\)-centered hydronickel \(\text{Ni}_4\text{H}_4\)X.\(^{10}\) O atoms, which link two B atoms, prove to be more effective bridges than both B and S in these complexes. The short O−Ni separation (\(\sim 2.2\) Å) indicates that weak electrostatic attraction exists between O and its neighboring Ni, but the interaction is not strong enough to form an effective chemical bond. It should be pointed out that the lowest vibrational frequencies (LVF) of both \(C_1\) (\(\text{Ni}_4\text{H}_3\text{N})_2\text{B}_2\text{O}_2^{2+}\)) and \((\text{Ni}_4\text{H}_3\text{C})_2\text{B}_2\text{O}_2\) are quite low (\(A_\text{u}\) modes, \(v = 12\) and \(18\) cm\(^{-1}\) for \(X = \text{C}\) and \(N\), respectively), indicating that these quasi-planar structures are vulnerable toward the \(A_\text{u}\) bending distortions along the long axes of the molecular plane. Further
analyses indicate that the low frequency mode of these molecules mainly involve either collective out-of-plane atomic movements in the same direction or in-plane atomic vibrations and therefore the approximate local planarity around the nonmetal centers is maintained in these vibrations. Limited available computing resources prevent us from performing more sophisticated investigations on these complexes at this stage.

Planar $D_{4h}$ Mg$_4$H$_4$C is a fourth-order stationary point with the biggest imaginary frequency of 506i cm$^{-1}$ and planar $C_{2h}$ (Mg$_4$H$_3$C)$_2$B$_2$O$_2$ possesses two imaginary frequencies at 138i ($A_u$) and 136i ($B_g$) cm$^{-1}$. The highest occupied molecular orbitals (HOMOs) of both the dumb-bell-shaped $C_{2h}$ (Mg$_4$H$_3$C)$_2$-B$_2$O$_2$ and (Mg$_4$H$_3$N)$_2$B$_2$O$_2^{2+}$ shown in Figure 3 are $\pi$ orbitals ($A_u$) mainly composed of the $p_z$ orbitals of N and C centers. But the delocalized $\pi$ bond is not strong enough to prevent C atoms from the out-of-plane distortions in both the $A_u$ and $B_g$ modes. N atoms, which are smaller in size than C, however, can be better accommodated in the Mg$_4$ cavities. Planar $C_{2h}$ (Mg$_4$H$_3$N)$_2$B$_2$O$_2^{2+}$ proves to be a true minimum with the LVF of 25 cm$^{-1}$ ($A_u$ mode). It should be noticed that, different from the Ni-containing complexes discussed above, O atoms in Mg-containing complexes also form an effective bond with neighboring Mg. The O–Mg bond is stronger than the O–Ni interaction because Mg and O atoms here carry much higher

Figure 1. Optimized structures of $C_1$ (Ni$_4$H$_3$C)$_2$B$_2$O$_2$ and (Ni$_4$H$_3$N)$_2$B$_2$O$_2^{2+}$, compared with $D_{4h}$ Ni$_4$H$_4$C and $D_{2h}$ B$_2$O$_2$ at B3LYP/6-311+G(d,p) level.

Figure 2. Optimized structures of $C_{2h}$ (Mg$_4$H$_3$C)$_2$B$_2$O$_2$ and (Mg$_4$H$_3$N)$_2$B$_2$O$_2^{2+}$, $D_{2h}$ (Mg$_4$H$_3$C)$_2$, and $D_{2h}$ (Mg$_4$H$_3$C)$_2$S$_2$, compared with $D_{4h}$ Mg$_4$H$_4$C at B3LYP-6-311+(d,p).
opposite charges than Ni and O and therefore the interactions between the former are more effective.

S atoms can be used as bridges in planar $D_{2h}$ (Mg$_4$H$_3$C)$_2$B$_2$O$_2$, which has the LVF of 22 cm$^{-1}$(B$_{3b}$). This structure obtains extra stabilities from the B$_{2g}$ π HOMO composed of mainly contributions of the p$_z$ orbitals of the C centers. As can be seen from Figure 3, this center-symmetrical bond is delocalized over the two separated Mg$_4$H$_3$C units. Two Mg$_4$H$_3$C units can also be connected by direct Mg—Mg interaction in (Mg$_4$C$_2$) (see Figure 2), which has the LVF of 32 cm$^{-1}$. Here the bridging Mg—Mg distance of 2.97 Å is obviously longer than the averaged Mg—Mg bond length of 2.69 Å. The $\sigma$ HOMO along the periphery of the six-membered Mg$_4$C$_2$ ring (see Figure 3), which involves mainly the contribution of the sp hybrids of the bridging Mg atoms, is critical in stabilizing the planarity of this complex.

Natural bond orbital (NBO) analyses indicate that effective charge-transfer exists in $C_{2v}$ (Mg$_4$H$_3$N)$_2$B$_2$O$_2$ and (Mg$_4$H$_3$C)$_2$B$_2$O$_2$ and the bonding in these complexes exhibits obvious ionic characteristics. Atoms in (Mg$_4$H$_3$N)$_2$B$_2$O$_2$ carry the charges Mg$_+1.60$, N$_{-2.77}$, B$_+0.41$, O$_{-1.14}$, and H$_{-0.72}$ [e], respectively, with the electronic configurations of Mg [Ne]$3d^{0.40}$, N[He]$2s^{1.90}$,$2p^{1.96}$,$2s^{1.96}$, and H $1s^{1.72}$. Atomic charges of (Mg$_4$H$_3$C)$_2$B$_2$O$_2$ are Mg$_+1.56$, C$_{-3.48}$, B$_+0.37$, O$_{-1.14}$, and H$_{-0.74}$ [e], with the electronic configurations of Mg[Ar]$-3s^{0.33}$, C[He]$2s^{1.82}$,$2p^{1.89}$, B[He]$2s^{1.88}$,$2p^{1.88}$, and H $1s^{1.74}$. C and N atoms in these complexes serve as the negative charge centers whereas the 3s electrons of Mg ligands are mostly transferred to the nonmetal centers and H bridging atoms. As indicated by the atomic charges of Ni$_{+0.66}$—0.77, N$_{-0.80}$, B$_{+0.64}$, O$_{-0.93}$, and H$_{-0.37}$ [e] in C$_2$ (NiH$_3$N)$_2$B$_2$O$_2$ and Ni$_{+0.42}$—0.48, C$_{-0.57}$, B$_{+0.64}$, O$_{-0.96}$, and H$_{-0.32}$ in C$_2$ (NiH$_3$C)$_2$B$_2$O$_2$, the charge transfer in Ni-containing complexes is much less effective than that in Mg-containing systems. This charge reduction is clearly reflected in the lower occupancies of Ni[He]$_{2s^{1.60}}$,$2p^{1.07}$ and H $1s^{1.25}$ in C$_2$ (NiH$_3$N)$_2$B$_2$O$_2$ and C[He]$_{2s^{1.49}}$,$2p^{1.03}$ and H $1s^{1.32}$ in C$_2$ (NiH$_3$C)$_2$B$_2$O$_2$ when compared to the electronic configurations of Mg-containing systems discussed above. It should also be pointed out that the bond parameters, charge distributions, and electron configurations of the Ni-containing complexes obtained in this work are very similar to the situation observed in monomer Ni$_4$H$_8$X$_{10}$. We have presented theoretical evidence of double TPN centers coexisting in one planar molecule in this work. Based upon this prediction, it is possible that TPNs could exist in salts such as [Ni$_4$H$_3$N]$_2$B$_2$O$_2$Cl$_2$ and [Mg$_4$H$_3$N]$_2$B$_2$O$_2$Cl$_2$, in which the counterions Cl$^-$ are expected to further stabilize these complexes. It will also be interesting to construct complexes containing multiple TPNs. Stable rings containing more than two B atoms in sp$^2$ hybrids are expected to serve as possible bridges. Describing the bonding nature between metal ligands (especially between transition metal ligands) involved in these complexes remains a huge challenge in theoretical chemistry.

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References and Notes