(M$_4$H$_3$X)$_2$B$_2$O$_2$: Hydrometal Complexes (M = Ni, Mg) Containing Double Tetracoordinate Planar Nonmetal Centers (X = C, N)

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Geometrical optimizations and electronic structural analyses of the −O$_2$B$_2$− bridged hydrometal complexes (M$_4$H$_3$C)$_2$B$_2$O$_2$ and (M$_4$H$_3$N)$_2$B$_2$O$_2$$^{2+}$ (M = 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.

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 D_{4h} Al$_4$C$^-$,[2] C_{2v} Al$_3$XC, Al$_3$XC$^-$(X = Si, Ge),[3,4] and [CAl$_4$]$^{2-}$.[5] Its analogues, tetracoordinate planar silicon and germanium, were observed in MAl$_4$ and MAl$_4$$^-$.[6] Density functional theory (DFT) investigations on penta- and hexacoordinate planar carbons were also reported recently.[7,8] Inspired by the recent proposal of hydrocoppers Cu$_n$H$_n$ (n = 3−6),[9] our group predicted very recently the existence of squared hydrometal complexes M$_4$H$_4$X centered with tetracoordinate planar nonmetals (TPN) (M = Ni, Cu; X = B, C, N, O).[10] This finding extends TPN centers from group IV atoms to include B, N, and O and the ligands from p block elements to d block transition metals including Ni and Cu. Taking M$_4$H$_4$X as building units, in this work, we explore the possibility of constructing hydrometal complexes containing double TPN centers. As we know, there have been no systems containing double TPC or other TPN centers reported in the literature to date.

Searching for suitable atoms or groups of atoms to bridge the building units proves to be the most difficult step in constructing such complexes. To satisfy the electronic requirements while keeping the planarity of the systems, we design bridges that possess atoms with unpaired electrons or singly occupied hybrid orbitals to replace bridging H on M$_4$ rings and are stable enough to hold two building units together. The fourmembered diradical −O$_2$B$_2$−, a rhombus with two B atoms at the two ends of the short diagonal, appears to serve this purpose, similar to the B$_4$ bridge incorporated in B$_4$(CO)$_2$.[11] Replacing Ni atoms with Mg, we find that hydromagnesium Mg$_4$H$_4$X can also be used to form similar complexes containing two TPN centers.

The DFT-B3LYP procedure implemented in the Gaussian 03 program[12] was employed in this investigation. Various initial structures were optimized at the B3LYP/Lanl2dz level first. Further optimizations were performed at B3LYP/6-311+G(d,p) and imaginary frequencies checked at the same theoretical level. The D_{2h} B$_2$O$_2$ bridge defined in this work is a rhombus with the B−B diagonal of 1.72 Å and the lowest vibration frequency

of 544 cm^{-1} (B$_{3u}$ mode). It underwent structural expansions and distortions when coupled into the complexes to be investigated. Both planar D_{2h} (Ni$_4$H$_3$N)$_2$B$_2$O$_2$$^{2+}$ and (Ni$_4$H$_3$C)$_2$B$_2$O$_2$ containing the bridge are found to have no imaginary frequencies at B3LYP/Lanl2dz, but the latter turns out to have two imaginary frequencies at B3LYP/6-311+G(d,p). Gradually reducing the symmetry of the molecule from D_{2h} to C_{2h} and finally to C_i produced a slightly distorted center-symmetrical (Ni$_4$H$_3$C)$_2$B$_2$O$_2$ with no imaginary frequency. In this C_i structure, one C atom is located 0.025 Å above the molecular plane and the other lies 0.025 Å below. It is slightly more stable than the perfect planar C_{2h} structure. But the energy difference between them is smaller than their difference in zero point energies. Therefore, the vibrationally averaged C_i (Ni$_4$H$_3$C)$_2$B$_2$O$_2$ is actually planar and has the approximate symmetry of C_{2h}, similar to the situation observed in the quasi-planar Al$_4$C$^-$.[2] −S− bridges and direct Mg−Mg bonding can also be utilized to stabilize the hydromagnesium complexes D_{2h} (Mg$_4$H$_3$C)$_2$. Figures 1 and 2 depict the B3LYP/6-311+G(d,p) structures obtained in this work with important bond lengths indicated, compared with the geometries of D_{4h} Ni$_4$H$_4$C, D_{4h} Mg$_4$H$_4$C, and D_{2h} B$_2$O$_2$ optimized at the same theoretical level.

As can be seen from Figure 1, B atoms, which replace an H in each Ni$_4$H$_4$X and link the two building units through the rhombus −B$_2$O$_2$−, play a central role in maintaining the planarity of both C_i (Ni$_4$H$_3$N)$_2$B$_2$O$_2$$^{2+}$ and (Ni$_4$H$_3$C)$_2$B$_2$O$_2$. B utilizes one of its three sp^2 hybrids to form a two-electron threecenter bond with two neighboring Ni atoms whereas the other two hybrids participate in the formation of the two B−O bonds in the B$_2$O$_2$ bridge. Maintaining the eight 2e−3c bonds along the peripheries of the two Ni$_4$ rings is confirmed to be important in stabilizing these complexes, as in the cases of X-centered hydronickel Ni$_4$H$_4$X.[10] O atoms, which link two B atoms, prove to be more effective bridges than both B and S in these complexes. The short O−Ni separation (∼2.2 Å) indicates that weak electrostatic attraction exists between O and its neighboring Ni, but the interaction is not strong enough to form an effective chemical bond. It should be pointed out that the lowest vibrational frequencies (LVF) of both C_i (Ni$_4$H$_3$C)$_2$B$_2$O$_2$ and C_i (Ni$_4$H$_3$N)$_2$B$_2$O$_2$$^{2+}$ are quite low (A$_u$ modes, v = 12 and 18 cm^{-1} for X = C and N, respectively), indicating that these quasiplanar structures are vulnerable toward the A$_u$ bending distortions along the long axes of the molecular plane. Further
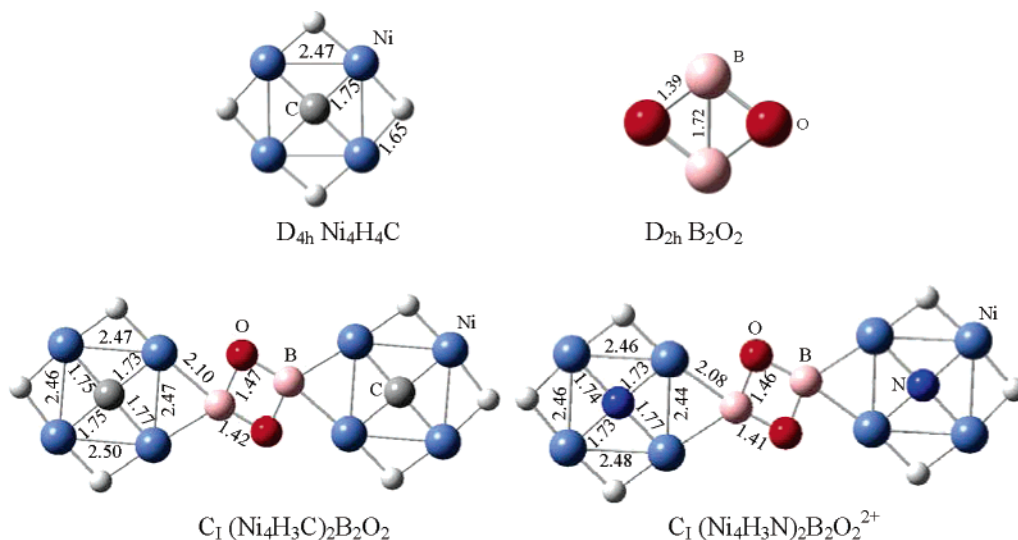
Figure 1. Optimized structures of C_i (Ni$_4$H$_3$C)$_2$B$_2$O$_2$ and (Ni$_4$H$_3$N)$_2$B$_2$O$_2$$^{2+}$, compared with D_{4h} Ni$_4$H$_4$C and D_{2h} B$_2$O$_2$ at B3LYP/6-311+G(d,p) level.
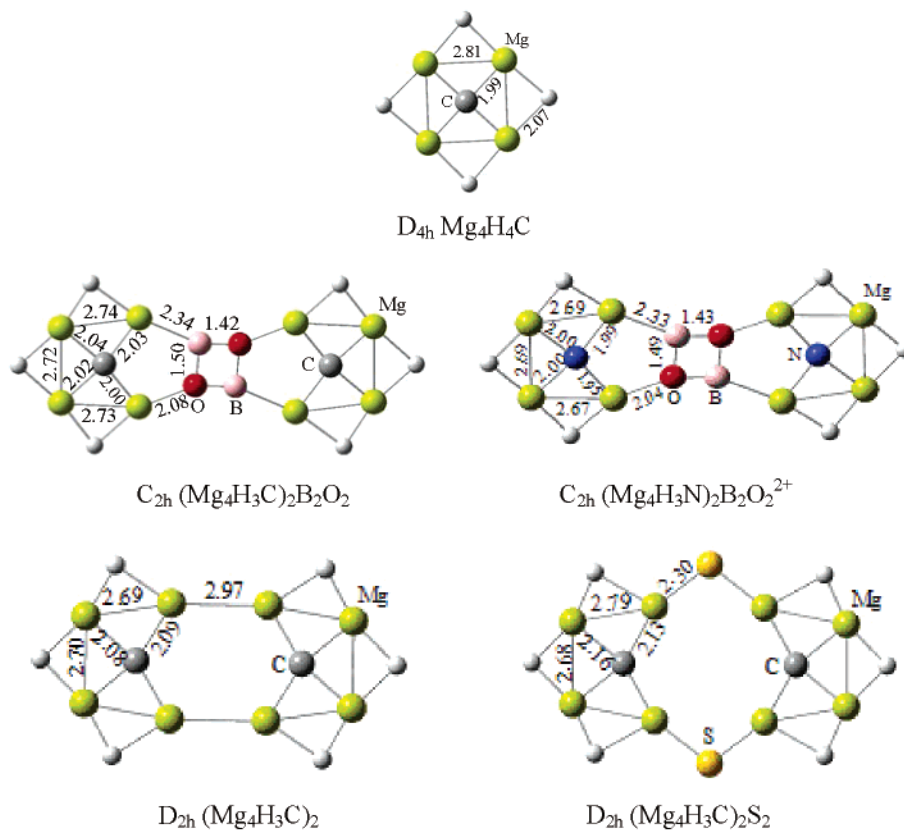
Figure 2. Optimized structures of C_{2h} (Mg$_4$H$_3$C)$_2$B$_2$O$_2$ and (Mg$_4$H$_3$N)$_2$B$_2$O$_2$$^{2+}$, D_{2h} (Mg$_4H_3$C)$_2$, and D_{2h} (Mg$_4H_3$C)$_2S_2$, compared with D_{4h} Mg$_4$H$_4$C at B3LYP-6-311+(d,p).

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$$^{2+}$ shown in Figure 3 are π orbitals (A$_u$) mainly composed of the p_z orbitals of N and C centers. But the delocalized π bond is not strong enough to prevent C atoms from the out-of-plane distortions in both the A$_u$ and B$_g$ modes. N atoms, which are smaller in size than C, however, can be better accommodated in the Mg$_4$ cavities. Planar C_{2h} (Mg$_4$H$_3$N)$_2$B$_2$O$_2$$^{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
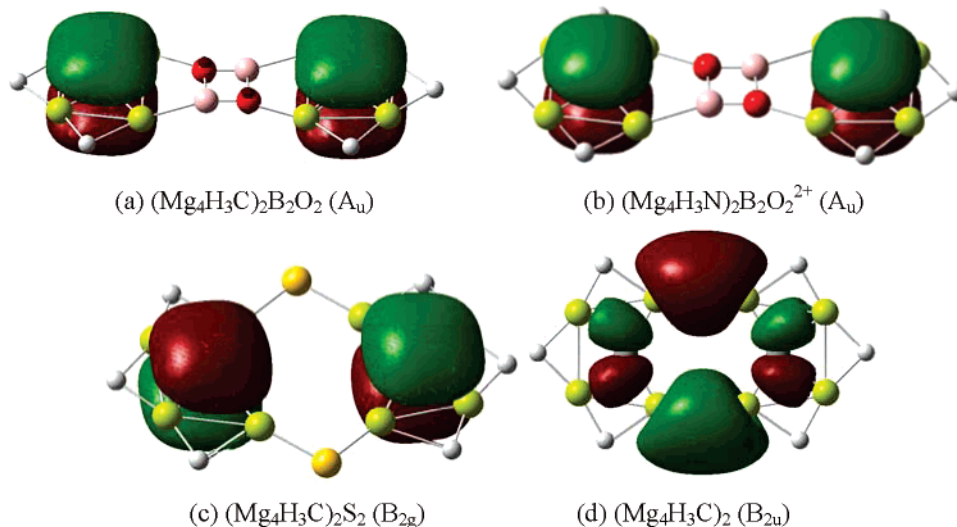
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(a) $(Mg_4H_3C)_2B_2O_2$ (A_u)

(b) $(Mg_4H_3N)_2B_2O_2{}^{2+}$ (A_u)

(c) $(Mg_4H_3C)_2S_2$ (B_{2g})

(d) $(Mg_4H_3C)_2$ (B_{2u})

Figure 3. HOMO pictures of (a) C_{2h} $(Mg_4H_3C)_2B_2O_2$, (b) C_{2h} $(Mg_4H_3N)_2B_2O_2{}^{2+}$, (c) D_{2h} $(Mg_4H_3C)_2S_2$, and (d) D_{2h} $(Mg_4H_3C)_2$ at B3LYP/6-311+G(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} $(Mg_4H_3C)_2S_2$, which has the LVF of 22 cm^{-1}(B_{3u}). 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_4H_3C units. Two Mg_4H_3C units can also be connected by direct Mg−Mg interaction in $(Mg_4H_3C)_2$ (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 σ HOMO along the periphery of the six-membered Mg_4C_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_{2h} $(Mg_4H_3N)_2B_2O_2{}^{2+}$ and $(Mg_4H_3C)_2$-B_2O_2 and the bonding in these complexes exhibits obvious ionic characteristics. Atoms in $(Mg_4H_3N)_2B_2O_2{}^{2+}$ 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]3s$^{0.40}$, N[He]2s$^{1.90}$2p$_x$$^{1.95}$2p$_y$$^{1.96}$2p$_z$$^{1.95}$, and H 1s$^{1.72}$. Atomic charges of $(Mg_4H_3C)_2B_2O_2$ are Mg +1.56, C −3.48, B +0.37, O −1.14, and H −0.74 |e|, with the electronic configurations of Mg[Ar]-3s$^{0.33}$, C[He]2s$^{1.83}$2p$_x$$^{1.89}$2p$_y$$^{1.88}$2p$_z$$^{1.86}$, and H 1s$^{1.74}$. C and N atoms in these complexes serve as the negative charge centers whereas the 3s^2 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 −0.27 |e| in C_i $(Ni_4H_3N)_2B_2O_2{}^{2+}$ and Ni +0.42−0.48, C −0.57, B +0.64, O −0.96, and H −0.32 in C_i $(Ni_4H_3C)_2B_2O_2$, 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 N[He]2s$^{1.69}$2p$^{4.07}$ and H 1s$^{1.25}$ in C_i $(Ni_4H_3N)_2B_2O_2{}^{2+}$ and C[He]2s$^{1.49}$2p$^{3.03}$ and H 1s$^{1.32}$ in C_i $(Ni_4H_3C)_2B_2O_2$ 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_4H_4X.[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 $[Ni_4H_3N]_2B_2O_2Cl_2$ and $[Mg_4H_3N]_2B_2O_2Cl_2$, 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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