

Tetracoordinate Planar Nonmetals

M₄H₄X: Hydrometals (M = Cu, Ni) Containing Tetracoordinate Planar Nonmetals (X = B, C, N, O)**

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Tetracoordinate planar carbon (that is, carbon atoms coordinated by four other atoms in a square-planar arrangement), first proposed by Hoffmann et al.^[1] over thirty years ago, was recently observed in the vibrationally averaged D_{4h} [Al₄C][−],^[2] C_{2v} Al₃XC, [Al₃XC][−] (X = Si, Ge),^[3,4] and [CAI₄]^{2−}.^[5] Tetracoordinate planar (TP) Si and Ge centers were also discovered in MAI₄ and [MAI₄][−].^[6] The TP bonding character of Group 14 elements, contrary to the conventional concept of tetrahedral C, Si, and Ge, is supported by excellent agreements between the measured photoelectron spectra and ab initio vertical detachment energies (VDE) of these molecules in the TP structures.

Here we extend the range of TP centers to include B, N, and O and the ligands from p-block elements to d-block

transition metals (Cu and Ni). On the basis of ab initio optimization results, we present the first theoretical evidence that, in the form of the X-centered hydrometals M₄H₄X, these first-row nonmetals X (X = B, C, N, O) are tetracoordinated by four transition-metal ligands M (M = Cu, Ni) in perfect squares. Hydrocopper Cu₄H₄ and hydronickel Ni₄H₄ are found to be suitable for hosting these tetracoordinate planar nonmetals (TPNs) with the high symmetry of D_{4h} . To the best of our knowledge, neither experimental nor theoretical data on these unusual molecules are available to date. Our work was stimulated by the proposal of aromatic hydrocopper Cu₄H₄ at the DFT level.^[7]

Various initial structures obtained at the B3LYP/Lanl2dz level were optimized at the B3LYP/6-311 + G(3df,p) level, and imaginary frequencies were checked at the same level. The DFT binding energies of 23.1 eV for D_{4h} Ni₄H₄C and 18.7 eV for C_{4v} Cu₄H₄C demonstrate the stability of these complexes with respect to dissociation. The B3LYP geometries were further refined with the second-order Møller–Plesset (MP2) procedure. We calculated the NMR shielding tensors using the gauge-independent atomic orbital (GIAO) procedure^[8,9] at the B3LYP/6-311 + G(3df,p) level, and VDEs, ionization potentials (IPs), and electron affinities (EAs) utilizing the restricted outer valence Green function method (ROVGF)^[10,11] with a smaller basis of 6-31 + G(d,p). The optimized MP2 bond parameters, normal vibrational frequencies, and electronic properties of these systems are provided in the Supporting Information. All the calculations were performed with the Gaussian03 program.^[12]

The optimized structures and corresponding HOMOs of the Cu₄H₄X series at the B3LYP level are depicted and compared with that of Cu₄H₄ in Figure 1a. The MP2 bond lengths were found to be about 5% shorter than the corresponding B3LYP values. Both [Cu₄H₄N]⁺ and [Cu₄H₄O]²⁺ have D_{4h} minima with TP N and TP O at the centers of the molecules. Their pyramidal (C_{4v}) and butterfly (D_{2d}) isomers are converted to the D_{4h} minima automatically during structural optimization, and other structures are either much higher in energy or high-order stationary points. Planar D_{4h} [Cu₄H₄B][−] and Cu₄H₄C, on the other hand, were found to be transition states with imaginary frequencies of 266i and 135i cm^{−1}, respectively, and lie 0.962 and 0.124 eV higher in energy than the corresponding tetracoordinate pyramidal C_{4v} structures. These imaginary frequencies correspond to the A_{2u} vibrational mode, in which the central atom X moves up and down along the fourfold axis. Distortion of the D_{4h} structure in the A_{2u} mode leads to the C_{4v} global minimum, in which the X atom lies about 0.5 Å above the Cu₄ plane. Note that the HOMOs of both D_{4h} [Cu₄H₄N]⁺ and [Cu₄H₄O]²⁺ feature delocalized cyclic σ bonds along the -Cu-H-Cu- peripheries. This characteristic bond plays a critical role in stabilizing the D_{4h} structures of [Cu₄H₄N]⁺ and [Cu₄H₄O]²⁺, and it is clearly inherited in the pyramidal C_{4v} ground states of both [Cu₄H₄B][−] and Cu₄H₄C, in which the nearly pure lone pair of 2p_z electrons of the central atom (discussed in detail below) overlaps partially with the cyclic σ bond. However, a cyclic σ HOMO does not exist in the D_{4h} transition states of Cu₄H₄C and [Cu₄H₄B][−], which have Cu–H separations greater than 1.700 Å. Instead of forming delocalized cyclic σ bonds, both

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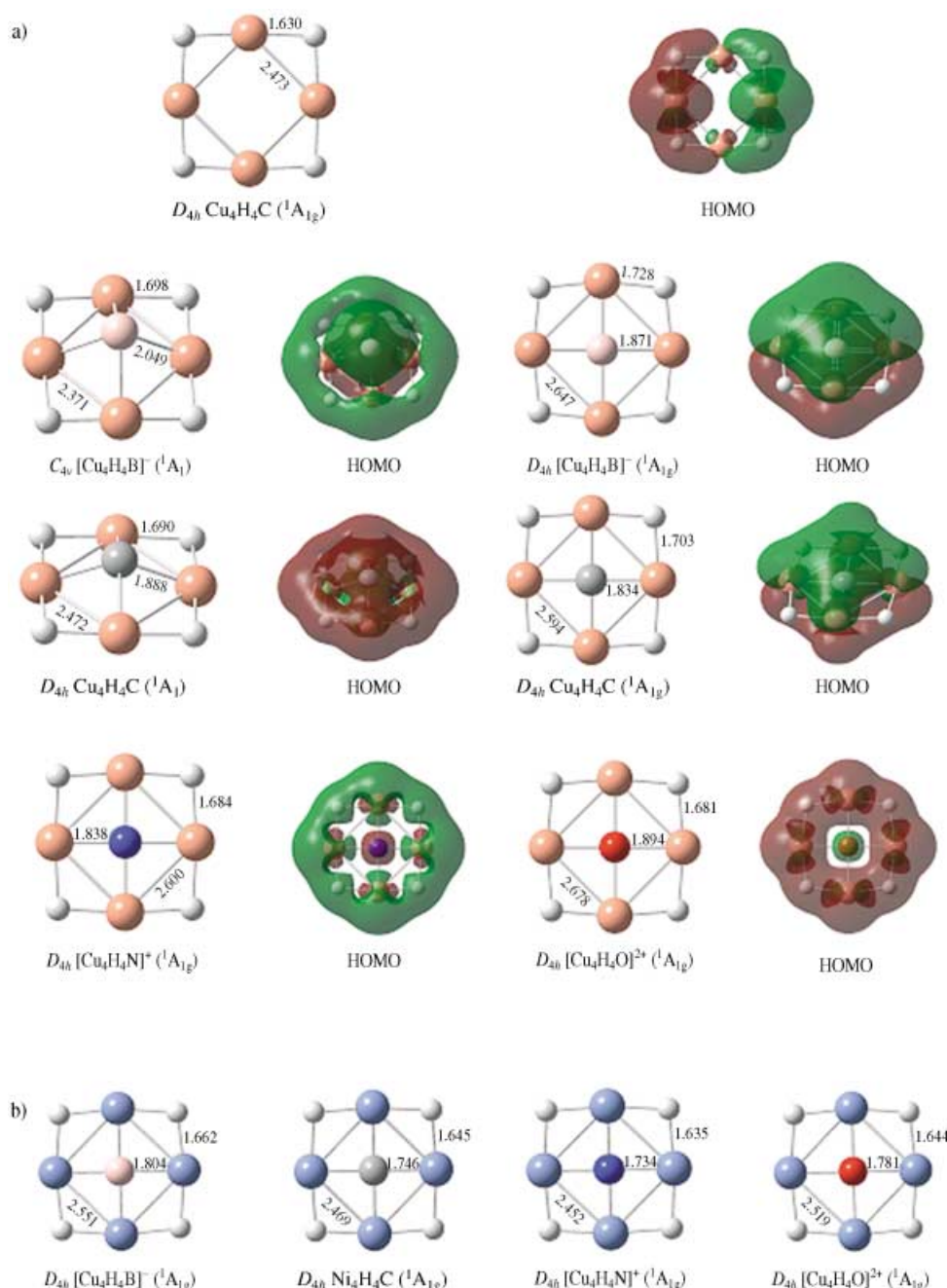


Figure 1. a) Optimized structures of the $\text{Cu}_4\text{H}_4\text{X}$ series and their corresponding HOMOs, compared with those of hydrocopper Cu_4H_4 ; b) optimum structures of D_{4h} $\text{Ni}_4\text{H}_4\text{X}$ ($\text{X} = \text{B}, \text{C}, \text{N}, \text{O}$) at the B3LYP/6-311 + G(3df,p) level.

planar D_{4h} $\text{Cu}_4\text{H}_4\text{C}$ and $[\text{Cu}_4\text{H}_4\text{B}]^-$ feature delocalized π HOMOs composed purely of contributions from the four Cu ligands and X center. This π interaction is not strong enough to prevent the D_{4h} planar structure from being distorted along the A_{2u} mode.

Natural bond orbital (NBO) analyses indicate that, in both D_{4h} and C_{4v} ground states, there is considerable electron transfer from the Cu ligands to the more electronegative center X, and the interactions between them exhibit clear ionic characteristics. For example, D_{4h} $[\text{Cu}_4\text{H}_4\text{N}]^+$ has atomic charges of Cu +1.00, N -1.62, and H -0.34 $|e|$ and the atomic charges of C_{4v} $\text{Cu}_4\text{H}_4\text{C}$ are Cu +0.87, C -1.83, and

H -0.41 $|e|$. In the transition states of D_{4h} $[\text{Cu}_4\text{H}_4\text{B}]^-$ and $\text{Cu}_4\text{H}_4\text{C}$, B and C carry even higher negative charges of -2.57 and -2.06 $|e|$ respectively. More detailed analysis shows that the central atoms X have three sp^2 hybrids and a nearly pure lone pair of $2p_z$ electrons perpendicular to the Cu_4 plane. For instance, the N atom in D_{4h} $[\text{Cu}_4\text{H}_4\text{N}]^+$ has the electron configuration $[\text{He}]2s^{1.95}2p_x^{1.32}2p_y^{1.32}2p_z^{1.96}$, and C in C_{4v} $\text{Cu}_4\text{H}_4\text{C}$ has $[\text{He}]2s^{1.92}2p_x^{0.92}2p_y^{0.92}2p_z^{1.85}$, with both $2p_z$ atomic orbitals nearly fully filled. This observation is in line with Hoffmann's proposal^[1] that the TP C in planar CH_4 has a pure lone pair of $2p_z$ electrons and there is considerable electron transfer from ligands H to central atom C.

The coordination chemistry of X-centered hydronickel $\text{Ni}_4\text{H}_4\text{X}$ is simpler. All the first-row nonmetals $\text{X} = \text{B}, \text{C}, \text{N}$, and O can be nicely fitted at the center of hydronickel Ni_4H_4 to form TPN centers (Figure 1b), and all these D_{4h} structures were confirmed to be true minima with no imaginary frequency. The NBO occupancy analyses indicate that, compared to Cu–X interactions, Ni–X bonds exhibit more covalent characteristics, except for Ni–O. This bonding feature is also supported by the observation that the nonmetal centers in D_{4h} $\text{Ni}_4\text{H}_4\text{X}$ have much smaller negative charges than those in $\text{Cu}_4\text{H}_4\text{X}$. For example, the N center in D_{4h} $[\text{Ni}_4\text{H}_4\text{N}]^+$ carries a negative charge of $-0.79 |e|$, about half the corresponding value of $-1.62 |e|$ in D_{4h} $[\text{Cu}_4\text{H}_4\text{N}]^+$. In D_{4h} $\text{Ni}_4\text{H}_4\text{C}$, which represents the first TP carbon atom at the center of a perfect square of transition-metal atoms, Ni, C, and H atoms carry atomic charges of $+0.47$, -0.55 , and $-0.33 |e|$ and have electron configurations of $\text{Ni}[\text{Ar}]4s^{0.30}3d^{1.22}$, $\text{C}[\text{He}]2s^{1.49}2p^{3.01}$, and $\text{H} 1s^{1.33}$, respectively. Here, the C center bears less than one-third of the negative charge of $-1.83 |e|$ it carries in C_{4v} $\text{Cu}_4\text{H}_4\text{C}$. This charge distribution shows that the transfer of valence electrons from Ni to X is much less effective than that from Cu. The reduced charge transfer is partially reflected in the low occupancies of the $2p_z$ orbitals of the central atoms. For instance, B, C, N, and O centers in D_{4h} $\text{Ni}_4\text{H}_4\text{X}$ systems have the electronic configurations of $\text{B}[\text{He}]2s^{1.20}2p_x^{0.84}2p_y^{0.84}2p_z^{0.39}$, $\text{C}[\text{He}]2s^{1.49}2p_x^{1.16}2p_y^{1.16}2p_z^{0.68}$, $\text{N}[\text{He}]2s^{1.69}2p_x^{1.48}2p_y^{1.48}2p_z^{1.09}$, and $\text{O}[\text{He}]2s^{1.84}2p_x^{1.73}2p_y^{1.73}2p_z^{1.55}$, respectively. The occupancies of the $2p_z$ orbitals increase quickly with increasing electronegativity of the central atoms. In addition, frequency analysis indicates that the H-bridged planar D_{4h} hydronickel Ni_4H_4 is a second-order transition state with two imaginary frequencies of $163i$ and $71i \text{ cm}^{-1}$. It is the introduction of an X atom at the center and the formation of four equivalent Ni–X interactions that stabilize the Ni_4H_4 square.

As nonmetal atoms X occupy the centers of heavy-atom squares in D_{4h} $\text{M}_4\text{H}_4\text{X}$, we checked the variation of relative NMR chemical shifts δ_H of the bridging H atoms in different systems to assess their aromaticity. Relative to the nuclear magnetic shielding tensor of H atoms (31.9 ppm) in T_d $\text{Si}(\text{CH}_3)_4$ (TMS), $\delta_H = -7.6$ ppm in benzene and -0.4 ppm in hydrocopper Cu_4H_4 , with both demonstrating the ring-current effect of aromatic systems. The bridging H atoms in the $\text{M}_4\text{H}_4\text{X}$ series, however, have positive δ_H values which show that these H atoms are located at higher field than $\text{Si}(\text{CH}_3)_4$ in NMR spectra. In the $\text{Cu}_4\text{H}_4\text{X}$ series, $\delta_H = +1.4$, $+1.2$, $+0.8$, and $+3.7$ ppm for $\text{X} = \text{B}, \text{C}, \text{N}$, and O , respectively. In the $\text{Ni}_4\text{H}_4\text{X}$ systems, the H atoms are shifted to even higher field. For instance, $\delta_H = +5.5$, $+4.3$, and $+3.2$ ppm for $\text{X} = \text{B}, \text{C}$, and N . These results are in line with $\delta_H = +0.6$ ppm for the two bridging H atoms in D_{2h} B_2H_6 . The upfield NMR chemical shifts of bridging H atoms outside the M_4 squares show that, unlike aromatic benzene and hydrocopper,^[7] $\text{M}_4\text{H}_4\text{X}$ systems are nonaromatic. Introducing an X atom at the molecular center breaks the ring current in Cu_4H_4 . These unusually high NMR chemical shifts could help to experimentally identify $\text{M}_4\text{H}_4\text{X}$ molecules frozen in suitable matrices.

The lowest two VDEs of $[\text{Cu}_4\text{H}_4\text{B}]^-$, the first IP and EA of $\text{Cu}_4\text{H}_4\text{C}$, and first EAs of $[\text{Cu}_4\text{H}_4\text{N}]^+$ and $[\text{Cu}_4\text{H}_4\text{O}]^{2+}$

calculated at the B3LYP and MP2 levels generally agree well and lie within the energy ranges of conventional photoelectron measurements. For instance, C_{4v} $[\text{Cu}_4\text{H}_4\text{B}]^-$ has the two lowest VDEs of 2.51 and 4.86 eV, while the corresponding values of the D_{4h} transition state are 2.13 and 3.98 eV. For C_{4v} $\text{Cu}_4\text{H}_4\text{C}$, IP = 8.46 and EA = 0.97 eV. Its D_{4h} transition state has IP = 9.40 and EA = 0.38 eV. These values can be used in identifying corresponding species and distinguishing different isomers by gas-phase photoelectron spectroscopy.

In summary, we have presented the first theoretical evidence for TPN atoms hosted at the centers of perfect squares of transition-metal atoms, which parallels the result obtained for TP carbon^[2] hosted at the center of an Al_4^{2-} square.^[13] Latest optimization results indicate that heterocyclic hydrometal systems $\text{Cu}_x\text{Ni}_y\text{H}_4$ ($x + y = 4$) with lower symmetries exhibit similar behavior. These predictions await experimental confirmation, which would open a new branch of chemistry of hydrometals with TPN centers that may have important applications as catalysts.

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