

D_{5h} $\text{Cu}_5\text{H}_5\text{X}$: Pentagonal Hydrocopper Cu_5H_5 Containing Pentacoordinate Planar Nonmetal Centers (X = B, C, N, O)

Si-Dian Li,^{*,[a]} Chang-Qing Miao,^[b] and Guang-Ming Ren^[b]

Keywords: Ab initio calculations / Density functional calculations / Hydrocopper / Pentacoordinate planar carbon / Electronic structures

Pentacoordinate planar nonmetals (PPNs) centered in perfect pentagonal hydrocopper complexes $\text{Cu}_5\text{H}_5\text{X}$ (X = B, C, N, O), as determined by density functional theory methods, are presented in this communication. The results obtained in this work complete the hypercoordinate planar carbon series

with high symmetries (D_{4h} , D_{5h} , and D_{6h}), and may shed new insight in catalyst chemistry.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

Exploring the bonding nature of carbon beyond the tetrahedral concept in organic chemistry has attracted considerable attention since Hoffmann et al.^[1] proposed the possibility of tetracoordinate planar carbon (TPC) thirty years ago. Recent experimental and theoretical investigations have confirmed the existence of TPCs in Al_4C^- with D_{4h} symmetry,^[2] Al_3XC and Al_3XC^- with C_{2v} symmetry (X = Si, Ge),^[3,4] and $[\text{CaL}_4]^{2-}$.^[5] A similar observation was reported for tetracoordinate planar Si and Ge in MAL_4 and MAL_4^- .^[6] Even more interesting, the possibility of pentacoordinate planar carbons (PPC) in $-\text{C}_3\text{B}_3-$, $-\text{C}_2\text{B}_4-$, and $-\text{CB}_5-$ subgroups and hexacoordinate planar carbons (HPCs) in B_6C^{2-} with D_{6h} symmetry was also explored by Schleyer et al.^[7–9] recently at the density functional theory (DFT) level. In a very recent paper,^[10] our group performed an ab initio investigation of tetracoordinate planar nonmetals (TPNs) centered in perfect square hydrometals M_4H_4 in D_{4h} $\text{M}_4\text{H}_4\text{X}$ complexes (X = B, C, N and O; M = Cu and Ni), and extended the tetracoordinate planar centers from carbon to other first-row nonmetal elements and the ligands from *p*-block elements to transition metal atoms. However, unlike D_{4h} TPCs and D_{6h} HPCs observed in simple molecules, a PPC center with a high D_{5h} symmetry is still missing. Here, we present theoretical investigations of pentacoordinate planar nonmetals (PPNs) in $\text{Cu}_5\text{H}_5\text{X}$ (X = B, C, N, O) complexes that contain D_{5h}

X centers in a perfect pentagonal hydrocopper (Cu_5H_5) proposed by Tsipis et al.^[11] To the best of our knowledge, there have been no investigations reported to date on D_{5h} PPCs or other TPNs centered in perfect pentagonal structures composed of transition metal ligands. The results obtained in this work complete the hypercoordinate planar carbon series with the high symmetries of D_{4h} , D_{5h} , and D_{6h} .

Initial structures obtained at DFT B3LYP/Lanl2d_z were further optimized at DFT B3LYP/6-311+G(3df,p) and imaginary frequencies were checked at the same level of theory.

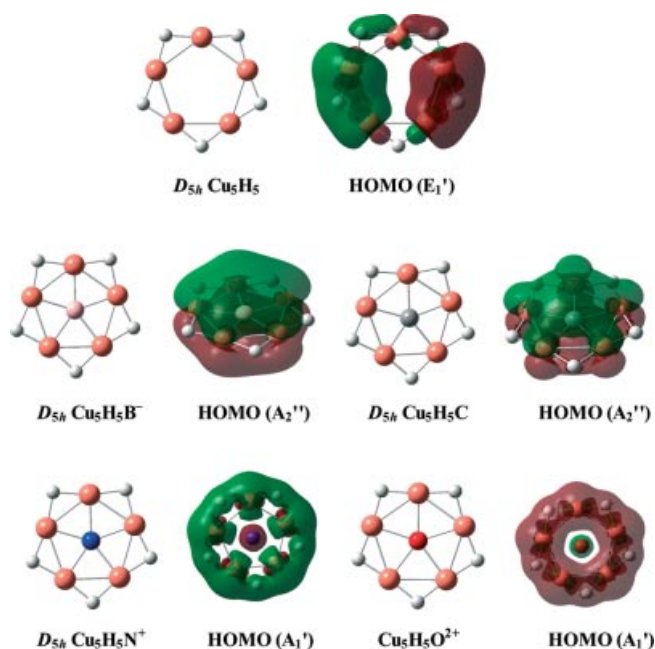


Figure 1. Optimized structures of D_{5h} $\text{Cu}_5\text{H}_5\text{X}$ complexes (X = B, C, N, O) and their HOMO diagrams compared with that of hydrocopper D_{5h} Cu_5H_5 at the B3LYP/6-311+G(3df,p) level

[a] Institute of Materials Sciences and Department of Chemistry, Xinzhou Teachers' University, Xinzhou 034000, Shanxi, P. R. China
Fax: (internat.) +86-0350-3031845
E-mail: lisidian@yahoo.com

[b] Institute of Materials sciences and Department of Chemistry, Xinzhou Teachers' University, Xinzhou 034000, Shanxi, P. R. China

Table 1. Optimized DFT bond lengths R , lowest vibrational frequencies $\nu_{\min}$ (cm⁻¹) and H NMR shielding tensors of D_{5h} Cu₅H₅X complexes (X = B, C, N, O); optimized bond lengths at MP2 are also listed for comparison

	Cu ₅ H ₅		Cu ₅ H ₅ B ⁻		Cu ₅ H ₅ C		Cu ₅ H ₅ N ⁺		Cu ₅ H ₅ O ²⁺	
	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
$R_{\text{Cu}-\text{Cu}}$ / Å	2.494	2.454	2.394	2.310	2.368	2.255	2.392	2.285	2.476	2.414
$R_{\text{Cu}-\text{H}}$ / Å	1.605	1.561	1.651	1.580	1.625	1.576	1.605	1.577	1.597	1.584
$R_{\text{Cu}-\text{X}}$ / Å			2.037	1.965	2.014	1.918	2.035	1.934	2.106	2.054
$\nu_{\min}$ / cm ⁻¹	63		57		52		49		52	
H NMR tensors / ppm	32.5		34.5		36.1		35.3		39.5	

The calculated binding energy $\Delta E = 255.7$ kJ/mol for the reaction $\text{Cu}_5\text{H}_5\text{C} = \text{Cu}_5\text{H}_5 + \text{C}$ clearly demonstrates the stability of the D_{5h} Cu₅H₅C with respect to dissociation to the hydrocopper Cu₅H₅ and the free C atom. When refined at the MP2/6-311+G(d,p) level of theory, the DFT bond lengths are systematically shortened by about 2 to 5%. The NMR shielding tensors were calculated using the gauge-independent atomic orbital (GIAO) procedure^[12] at the B3LYP/6-311+G(3df,p) level. The optimized DFT structures and corresponding highest occupied molecular orbital (HOMO) diagrams of the D_{5h} Cu₅H₅X series are depicted and compared with that of the pentagonal hydrocopper Cu₅H₅ at the same level of theory in Figure 1. The optimized bond parameters, lowest vibrational frequencies and NMR shielding tensors at DFT, and the bond lengths at MP2 are summarized in Table 1. All the calculations were performed using the Gaussian 03 suite of programs.^[13]

Different from the squared Cu₄H₄X series,^[10] all the isoelectronic Cu₅H₅X neutral and charged ions possess perfect planar pentagonal structures with the highest symmetry, D_{5h} (see Figure 1). As can be seen from Figure 1 of ref. 10,^[10] the Cu₄H₄ square is too small to accommodate the B and C centers. However, the Cu₅H₅ pentagon studied here is shown to have the correct size such that the first-row nonmetal centers (from B, C, N to O) can be accommodated to form D_{5h} Cu₅H₅X complexes without imaginary frequencies (see Table 1). In addition, structures with initial C_{5v} symmetry and off-plane X atoms along the fivefold axis are found to be automatically converted into perfect planar pentagons during structural optimization, further confirming that these D_{5h} complexes are true minima on their potential energy surfaces. Various initial structures with lower symmetries have also been tested; however, optimized structures with lower energies are not obtained. These high symmetry D_{5h} geometries with the lowest energies obtained in this work possess high stabilities as discussed above for D_{5h} Cu₅H₅C and have no imaginary frequencies that lead to structural distortions. The Cu–Cu separations in the Cu₅H₅X complexes are systematically shorter than those in the parent Cu₅H₅, but these distances increase from Cu₅H₅N⁺ to Cu₅H₅O²⁺. The bonding characteristics of the HOMOs of the complex series are clearly demonstrated in the molecular orbital diagrams shown in Figure 1. The molecular orbital analyses indicate that for Cu₅H₅B⁻ and Cu₅H₅C, the doubly occupied highest occupied molecular

orbitals (HOMOs) are delocalized π bonds (A_1') mainly composed of the $2p_z$ orbitals of the central atoms (with a slight contribution from the 3d orbitals of the Cu ligands), while the HOMOs of Cu₅H₅N⁺ and Cu₅H₅O²⁺ are delocalized σ bonds (A_2'') with the largest contribution from the 4s and 3d orbitals of the Cu ligands and partial contribution from the 2s orbitals of the central atoms. The delocalized σ HOMOs obtained here for Cu₅H₅N⁺ and Cu₅H₅O²⁺ are similar to the σ HOMOs observed in D_{4h} Cu₄H₄N⁺ and Cu₄H₄O²⁺.^[10]

Natural bond orbital (NBO) analyses give new insights into the understanding of the atomic charge distribution and electron configurations of these complexes. The NBO results indicate that in the Cu₅H₅X complexes the X atoms serve as the negatively charged nonmetal centers, the Cu atoms at the periphery form a positively charged ring, and the bridging H atoms carry negative charges to maintain the overall charge balance. For example, Cu₅H₅C has the atomic charges of C $-1.91|e|$, Cu $+0.79|e|$, and H $-0.41|e|$, and the corresponding values for Cu₅H₅B⁻ are B $-2.36|e|$, Cu $+0.72|e|$, and H $-0.44|e|$. Even in the positively charged Cu₅H₅N⁺ and Cu₅H₅O²⁺ structures, the N and O centers carry the negative charges of $-1.54|e|$ and $-1.19|e|$, the Cu atoms possess the positive charges of $+0.87|e|$ and $+0.96|e|$, and the H atoms have negative charges of $-0.37|e|$ and $-0.33|e|$, respectively. This “sandwich” charge distribution reflects the consequence of electron transfer from the Cu ligands to the nonmetal centers X and the bridging H atoms, and results in the nearly pure lone pairs of electrons in the $2p_z$ orbitals of the central atoms. The high occupancies of the $2p_z$ orbitals are clearly demonstrated in the atomic electron configurations of B[He]2s^{1.75}2p_x^{0.82}2p_y^{0.82}2p_z^{1.88}, C[He]2s^{1.86}2p_x^{1.05}2p_y^{1.05}2p_z^{1.92}, N[He]2s^{1.93}2p_x^{1.30}2p_y^{1.30}2p_z^{1.95}, and O[He] 2s^{1.97}2p_x^{1.60}2p_y^{1.60}2p_z^{1.97} in the corresponding complexes. It is interesting to note that in Cu₅H₅B⁻ and Cu₅H₅C the nearly doubly occupied $2p_z$ orbitals of the central atoms dominate the formation of the π -typed HOMOs, while in the positively charged Cu₅H₅N⁺ and Cu₅H₅O²⁺ structures, the $2p_z$ orbitals mainly participate in the formation of the molecular orbitals next to the HOMOs (HOMO–1), which are also π -typed orbitals (not shown in Figure 1). For all the D_{5h} TPNs studied in this work, the 2s, 2p_x, and 2p_y valence orbitals of the central atom form sp² hybrids to form five equivalent partial bonds with the periphery copper ligands.

The orbital hybridization pattern observed here for PPNs parallels those in the TPCs in planar D_{4h} CH_4 and $\text{Ni}_4\text{H}_4\text{C}$ structures, where the C center with three sp^2 hybrids forms equivalent bonds with its four equivalent ligands.^[1,10] These D_{4h} TPC and D_{5h} PPN structures are achieved by resonances between equivalent structures allowed by the hybridization patterns of the central atoms and the arrangements of the specific ligands around them, as discussed in the case of D_{4h} CH_4 .^[1]

In order to assess the aromaticity of $\text{Cu}_5\text{H}_5\text{X}$ complexes we observe the variation of the NMR spectroscopic chemical shifts of the H atoms relative to the NMR shielding tensor of the H atoms in tetrahedral $\text{Si}(\text{CH}_3)_3$ ($\delta = 31.9$ ppm), since the geometrical center of the Cu_5H_5 pentagon is occupied by a nonmetal center. For $\text{X} = \text{B}, \text{C}, \text{N}$ and O the calculated $\delta_{\text{H}} = +2.6, +4.2, +3.4$, and $+7.6$ ppm, respectively. These up-field chemical shifts calculated for the H atoms outside the Cu_5 ring clearly indicate that the ring current effects in Cu_5H_5 ^[11] vanish because of the introduction of the X atoms at the ring centers, and therefore the $\text{Cu}_5\text{H}_5\text{X}$ complexes studied here are nonaromatic in nature. This finding is in agreement with the results obtained for the $\text{M}_4\text{H}_4\text{X}$ series.^[10]

In this work we have presented ab initio evidence of PPCs and other PPNs centered in perfect pentagonal $\text{Cu}_5\text{H}_5\text{X}$ complexes. Investigations on heteropentagonal systems $\text{M}_x\text{M}'_y\text{H}_5\text{X}$ ($x + y = 5$) containing PPNs are under progress. Dimerization or formation of even higher aggregates are also possible, similar to the systems containing double HPCs.^[9] Hydrometal complexes centered with hypercoordinate planar nonmetals are important in fundamental research and could have important applications in catalyst chemistry.

Acknowledgments

This work was financially supported by The Shanxi Natural Science Foundation. S.-D. L. is grateful to Dr. Hai-Shun Wu, Xiao-

Hong Xu, and Hai-Jun Jiao for inspiring discussions and suggestions.

- [1] R. Hoffmann, R. W. Alder, C. F. Wilcox Jr., *J. Am. Chem. Soc.* **1970**, *92*, 4992.
- [2] X. Li, L.-S. Wang, A. I. Boldyrev, J. Simons, *J. Am. Chem. Soc.* **1999**, *121*, 6033.
- [3] L. S. Wang, A. I. Boldyrev, X. Li, J. Simons, *J. Am. Chem. Soc.* **2000**, *122*, 7681.
- [4] X. Li, H.-J. Zhai, L.-S. Wang, *Chem. Phys. Lett.* **2002**, *357*, 415.
- [5] X. Li, H.-F. Zhang, L.-S. Wang, G. D. Geske, A. I. Boldyrev, *Angew. Chem. Int. Ed.* **2000**, *39*, 3630.
- [6] A. I. Boldyrev, X. Li, L.-S. Wang, *Angew. Chem. Int. Ed.* **2000**, *39*, 3307.
- [7] Z.-X. Wang, P. v. R. Schleyer, *Science* **2001**, *292*, 2465.
- [8] K. Exner, P. v. R. Schleyer, *Science* **2000**, *290*, 1937.
- [9] Z.-X. Wang, P. v. R. Schleyer, *Angew. Chem. Int. Ed.* **2002**, *41*, 4082.
- [10] S.-D. Li, G.-M. Ren, C.-Q. Miao, Z.-H. Jin, *Angew. Chem. Int. Ed.* **2004**, *43*, 1371.
- [11] A. C. Tsepis, C. A. Tsepis, *J. Am. Chem. Soc.* **2003**, *125*, 1136.
- [12] R. Ditchfield, *Mol. Phys.* **1974**, *27*, 789; K. Wolinski, J. F. Hilton, P. Pulay, *J. Am. Chem. Soc.* **1990**, *112*, 8251.
- [13] Gaussian 03, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian Inc., Pittsburgh PA, **2003**.

Received March 20, 2004