

## Hydrometal Analogues of Aromatic Hydrocarbons: A New Class of Cyclic Hydrocoppers(I)

Athanasios C. Tsepis and Constantinos A. Tsepis\*

Laboratory of Applied Quantum Chemistry, Faculty of Chemistry, Aristotle University of Thessaloniki, 541 24 Thessaloniki, Greece

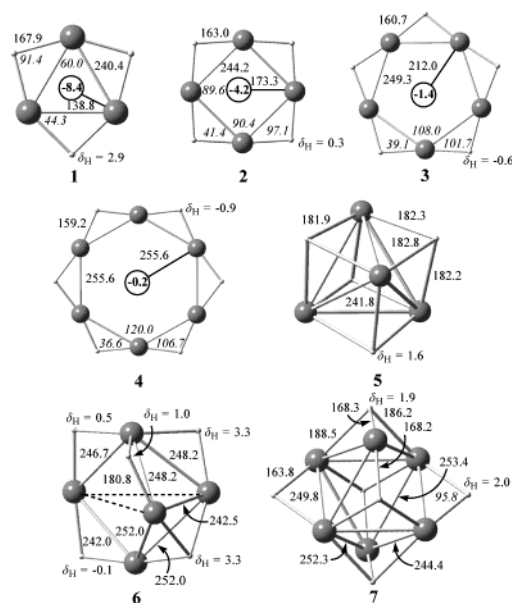
Received October 3, 2002; E-mail: tsepis@chem.auth.gr

The recent advance of the aromaticity concept into all-metal molecules containing  $Al_4^{2-}$ ,  $XAl_3^-$ ,  $Ga_4^{2-}$ ,  $In_4^{2-}$ ,  $Hg_4^{6-}$ ,  $Al_3^-$ , and  $Ga_3^-$  aromatic units<sup>1</sup> prompted us to explore the possibility for hydrometal analogues of the aromatic hydrocarbons. In effect, what we address here is a new class of cyclic copper(I) hydrides (hydrocoppers) formulated as  $Cu_nH_n$  ( $n = 3-6$ ) as the cyclic hydrocarbon analogues in the diverse tapestry of inorganic chemistry. Our choice of the copper(I) hydrides was based on the well-known tendency of copper(I) centers to cluster together in a variety of organocopper(I) compounds<sup>2</sup> involving even the alkyl groups as bridging ligands, a representative example being the cyclic  $Cu_4R_4$  tetramer.<sup>3</sup> In  $Cu_4R_4$  ( $R = CH_2SiMe_3$ ) the four Cu(I) atoms form a square planar four-membered ring with short Cu–Cu distances of 2.42 Å, while the four alkyl groups form four bridges just outside the square. Obviously, one may think that the hydride analogues could also be stable species for the hydride ligand exerts electronic effects similar to those of the alkyl ligands (both are isolobal pure  $\sigma$  donor ligands). Why the cyclic  $Cu_nH_n$  species are expected to be stable molecules and why they exhibit a perfect planar configuration are questions that we attempt to answer herein by means of quantum chemical calculations at the B3LYP level of theory<sup>4</sup> using the 6-311+G(d,p) and LANL2DZ basis sets as implemented in the Gaussian98 series of programs.<sup>5</sup> Noteworthy is the nonsensitivity of the structural and energetic parameters of the  $Cu_nH_n$  species to the basis set quality.

Selected geometric parameters for the cyclic  $Cu_nH_n$  ( $n = 3-6$ ) molecules computed at the B3LYP/6-311+G(d,p) level of theory are shown in Figure 1. Notice that in all clusters the hydride ligands bridge neighboring Cu(I) atoms, forming isosceles triangles. The Cu–H bond length found in the range of 162.1–171.3 pm is decreasing from the three- to six-membered all-metal rings. Noteworthy is the shortest Cu–H bond length of 148.8 pm computed for the CuH monomer which is in excellent agreement with the experimental value<sup>6</sup> of 146.5 pm.

A range of Cu–Cu distances is found in the computed structures, the shortest of 240.4 pm found in the cyclic  $Cu_3H_3$  hydrocopper, and the longest of 255.6 pm, in the six-membered all-metal ring. Interestingly all metallacycles adopt perfect planar configuration of high symmetry and can be considered as the all-metal analogues of the corresponding cyclic hydrocarbons. Noteworthy is the equivalence of the Cu–Cu and Cu–H bonds in the metallacycles which is indicative of the aromatic character of the cyclic hydrocoppers(I). With respect to the hydride ligands, copper adopts, except for  $Cu_3H_3$ , the preferred almost linear coordination.

All species are predicted to be bound with respect to their dissociation either to CuH monomer or to free Cu and H atoms in their ground states. The computed binding energies along with the NICS(0) and electrophilicity index  $\omega$  values are collected in Table 1.



**Figure 1.** Selected geometric parameters for the cyclic planar and cubic  $Cu_nH_n$  molecules computed at the B3LYP/6-311+G(d,p) level of theory.

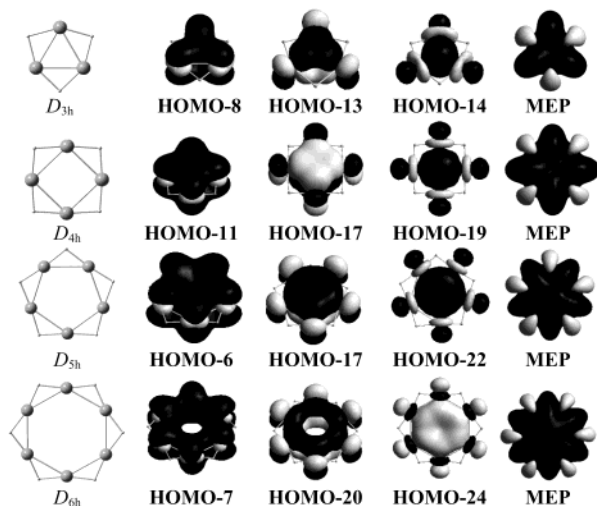
**Table 1.** Binding Energies  $\Delta E_1$  and  $\Delta E_2$  (in kcal mol<sup>-1</sup>), GIAO-SCF NICS (ppm) and Electrophilicity ( $\omega$ ) of the Cyclic  $Cu_nH_n$  Clusters ( $n = 3-6$ ) Computed at the B3LYP/6-311+G(d,p) Level

cluster	$\Delta E_1^a$	$\Delta E_2$	NICS	$\omega$
$Cu_3H_3$ , <b>1</b>	81.5	260.9	-8.4	1.595
$Cu_4H_4$ , <b>2</b>	137.0	376.1	-4.2	1.743
$Cu_5H_5$ , <b>3</b>	180.1	479.0	-1.4	2.040
$Cu_6H_6$ , <b>4</b>	217.5	576.2	-0.2	2.230

<sup>a</sup>  $\Delta E_1 = E(CuH)_n - nE(CuH)$ ;  $\Delta E_2 = E(CuH)_n - n[E(Cu) + E(H)]$ .

To check the reliability of the B3LYP results we computed the Cu–H bond dissociation energy of the CuH monomer and found the value of 59.8 kcal mol<sup>-1</sup> which is in excellent agreement with the experimental value<sup>7</sup> of 61(4) kcal mol<sup>-1</sup> and the previously reported theoretical values of 52.8, 60.9, 60.6 kcal mol<sup>-1</sup> computed at the SDCl, CPF, and MCPF levels of theory, respectively.<sup>8</sup>

Considering that solid CuH adopts a wurtzite structure, we have also searched the PES of  $Cu_nH_n$  species for stable nonplanar structures. In effect, we found on the PES of  $Cu_4H_4$ ,  $Cu_5H_5$ , and  $Cu_6H_6$  molecules local minima corresponding to 3D structures with the  $Cu_n$  ( $n = 4, 5, \text{ and } 6$ ) cores exhibiting tetrahedral ( $T_d$ ) **5**, trigonal bipyramidal ( $C_{2v}$ ) **6**, and octahedral ( $D_{2h}$ ) **7**, stereochemistry, respectively (Figure 1). In the  $T_d$  structure the hydride ligands are triply bonded to copper(I) atoms located over the center of each face of the tetrahedron. In the  $C_{2v}$  and  $D_{2h}$  structures only one- and two-hydride ligands are triply bonded to Cu atoms, respectively,



**Figure 2.** Selected highly delocalized molecular orbitals along with the molecular electrostatic potential (MEP) of the planar cyclic  $\text{Cu}_n\text{H}_n$  molecules contributing to aromaticity.

the rest being doubly bonded to adjacent copper(I) atoms. The 3D structures were found to be less stable than the planar ones by 46.4, 27.5 and 29.8 kcal mol<sup>-1</sup> for the  $\text{Cu}_4\text{H}_4$ ,  $\text{Cu}_5\text{H}_5$ , and  $\text{Cu}_6\text{H}_6$  molecules, respectively.

To understand the planarity and structural integrity of the cyclic  $\text{Cu}_n\text{H}_n$  molecules the most relevant valence molecular orbitals depicted schematically in Figure 2 have been analyzed.

Perusal of Figure 2 reveals that all metallacycle rings exhibit a composite bonding mode involving both  $\sigma$ ,  $\pi$ , and  $\delta$  components. Noteworthy is the presence of highly delocalized  $\pi$ - and  $\delta$ -type MOs, resulting from the bonding interaction of the 3d AOs of the ring Cu(I) atoms similar to the  $\pi$ -type MOs ( $p\pi$ - $p\pi$  overlap) of the corresponding aromatic hydrocarbons, which support a ring current (HOMO-8 and -13, HOMO-11 and -17, HOMO-6 and -17 and HOMO-7 and -20 for the three-, four-, five-, and six-membered rings, respectively). Moreover, there are also highly delocalized  $\sigma$ -type MOs resulting from the bonding interaction of the 3d AOs ( $d\sigma$ - $d\sigma$  overlap) of the ring Cu(I) atoms (HOMO-14, HOMO-19, HOMO-22 and HOMO-24 for the three-, four-, five-, and six-membered rings, respectively). The delocalized  $\sigma$  and  $\pi$  electron density in the rings could probably account for the observed equivalence of the Cu-Cu bonds. Planarity, high stability, and bond length equalization are conventionally good indicators of aromaticity, but this is restrictive in many examples. Moreover, the molecular electrostatic potential (MEP) being positive over the all-metal rings and negative on the hydride ligands strongly supports electrophilic substitution reactions, which are characteristic of the aromatic systems. To quantify the aromaticity/antiaromaticity of the cyclic hydrocoppers we applied the magnetic criterion, viz. nucleus-independent chemical shift (NICS) proposed by Schleyer et al.<sup>9</sup> NICS values, which are the negative of the absolute magnetic shielding tensors calculated at the ring or cage centers<sup>10</sup> are shown in Figure 1. It can be seen that all cyclic hydrocoppers exhibit negative NICS values, the absolute values decreasing along the series of the three- to six-membered all-metal rings. The lowering of the NICS values follows the reverse trend of the ring radius (Figure 1). It seems that NICS is dependent on the ring size; thereby, the low values for the five- and six-membered rings cannot exclude aromaticity for these systems. This is substantiated by the NICS values of -7.6, -4.6, -3.4, and 0.3 ppm of the substituted  $[\text{Cu}_3(\text{CH}_3)_3]$ ,  $[\text{Cu}_3(\text{NH}_2)_3]$ ,  $[\text{Cu}_3(\text{OH})_3]$ , and  $[\text{Cu}_3(\text{PH}_2)_3]$  derivatives with ring radii of 138.0, 150.8, 156.3, and 190.2 pm, respectively at the B3LYP/LANL2DZ level. The extent of aromaticity of the

$\text{Cu}_n\text{H}_n$  ( $n = 3-6$ ) molecules is also mirrored on the computed<sup>11</sup> electrophilicity index  $\omega = \mu^2/2\eta$ , where  $\mu$  and  $\eta$  are the chemical potential and hardness, respectively, given approximately by the expressions  $\mu = (\epsilon_{\text{LUMO}} + \epsilon_{\text{HOMO}})/2$  and  $\eta = (\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}})$ . Notice that the NICS of  $\text{Cu}_3\text{H}_3$  is comparable to that of  $\text{C}_6\text{H}_6$  (-9.7 ppm), while the  $\omega$  of  $\text{Cu}_6\text{H}_6$  is almost identical to that of  $\text{C}_6\text{H}_6$  (2.165 eV) computed at the same level of theory. The high stability of the three-, four-, and five-membered all-copper(I) rings is reflected on several structurally characterized complexes thus far involving the respective rings.<sup>2</sup>

**Supporting Information Available:** Cartesian coordinates for relevant structures optimized at various levels of theory, Tables S1, S2, and S3 showing natural orbital and Mulliken population analysis data, the NMR shielding tensor elements (ppm), and the harmonic vibrational frequencies (cm<sup>-1</sup>) of  $\text{Cu}_n\text{H}_n$  and  $\text{Cu}_3\text{X}_3$  ( $\text{X} = \text{CH}_3$ ,  $\text{NH}_2$ ,  $\text{OH}$ , and  $\text{PH}_2$ ) molecules, respectively, Figure S1 showing the equilibrium structures of the  $\text{Cu}_3\text{X}_3$  ( $\text{X} = \text{CH}_3$ ,  $\text{NH}_2$ ,  $\text{OH}$ , and  $\text{PH}_2$ ) molecules, and Figures S2-S5 providing an expanded list of MOs of the planar aromatic  $\text{Cu}_n\text{H}_n$  (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) (a) Boldyrev, A. I.; Kuznetsov, A. E. *Inorg. Chem.* **2002**, *41*, 532. (b) Li, X.; Kuznetsov, A. E.; Zhang, H. F.; Boldyrev, A. I.; Wang, L. S. *Science* **2001**, *291*, 859. (c) Li, X.; Zhang, H. F.; Wang, L. S.; Kuznetsov, A. E.; Cannon, N. A.; Boldyrev, A. I. *Angew. Chem., Int. Ed.* **2001**, *40*, 1867. (d) Kuznetsov, A. E.; Boldyrev, A. I.; Li, X.; Wang, L. S. *J. Am. Chem. Soc.* **2001**, *123*, 8825. (e) Kuznetsov, A. E.; Corbett, J. D.; Wang, L. S.; Boldyrev, A. I. *Angew. Chem., Int. Ed.* **2001**, *40*, 3369. (f) Jusélius, J. J.; Straka, M.; Sundholm, D. *J. Phys. Chem. A* **2001**, *105*, 9939. (g) Fowler, P. W.; Havenith, R. W. A.; Steiner, E. *Chem. Phys. Lett.* **2001**, *342*, 85. (h) Robinson, G. H. *Acc. Chem. Res.* **1999**, *32*, 773.
- (2) (a) Vega, A.; Calvo, V.; Spodine, E.; Zarate, A.; Fuenzalida V.; Sailard, J.-Y. *Inorg. Chem.* **2002**, *41*, 532. (b) Yam, V. W.-W.; Fung, W. K.-M.; Cheung, K.-K. *J. Cluster Sci.* **1999**, *10*, 37. (c) Yam, V. W.-W.; Fung, W. K.-M.; Cheung, K.-K. *Organometallics* **1998**, *17*, 3293. (d) Niemeyer, M. *Organometallics* **1998**, *17*, 4649 and references therein. (e) Hermann, E.; Richter, R.; Chau, N. Z. *Anorg. Allg. Chem.* **1997**, *623*, 403. (f) Eriksson, H.; Håkansson, M. *Organometallics* **1997**, *16*, 4243. (g) Eriksson, H.; Örtendhal, M.; Håkansson, M. *Organometallics* **1996**, *15*, 4823. (h) Yam, V. W.-W.; Lee, W.-K.; Lai, T.-F. *Organometallics* **1993**, *12*, 2383. (i) Knötter, D. M.; Grove, D. M.; Smeets, W. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1992**, *114*, 3400. (j) Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1990**, *112*, 8008. (k) Meyer, E. M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1989**, *8*, 1067.
- (3) Jarvis, J. A. J.; Kilbourn, B. T.; Pearce, R.; Lappert, M. F. *J. Chem. Soc. Chem. Commun.* **1973**, 475.
- (4) Details for the implementation of B3LYP: Becke, A. D. *J. Chem. Phys.* **1992**, *96*, 2125. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 907. In all computations no constraints were imposed on the geometry. Full geometry optimization was performed for each structure using Schlegel's analytical gradient method: Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.
- (5) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millan, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M.; Johnson, P.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian Inc.: Pittsburgh, PA, 1998.
- (6) Huber, K. P.; Herberg, G. *Molecular Spectra and Molecular Structure*; Van Nostrand Reinhold: New York, 1979.
- (7) Armentrout, P. B.; Beauchamp, J. L. *Acc. Chem. Res.* **1989**, *22*, 315.
- (8) Chong, D. P.; Langhoff, S. R.; Bauschlicher, C. W., Jr.; Walch, S. P.; Partridge, H. *J. Chem. Phys.* **1986**, *85*, 2850.
- (9) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jao, H.; Homes, N. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.
- (10) Absolute NMR shielding tensors were calculated at the B3LYP/6-311+G-(d,p) optimized geometries using the GIAO method: (a) Ditchfield R. *Mol. Phys.* **1974**, *27*, 789. (b) J. Gauss. *J. Chem. Phys.*, **1993**, *99*, 3629. NICS values were computed at the HF/6-31+G(d)//B3LYP/6-311+G-(d,p) level of theory.
- (11) Parr, R. G.; v. Szentpály, L.; Liu, S. *J. Am. Chem. Soc.* **1999**, *121*, 1922.

JA028786J