How the Aromatic 4-Membered Hydrido-Bridged Copper Rings Respond to Successive Nucleophilic Attack?

C.A. Tsipis[*] and N.D. Charistos

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

Abstract: Electronic structure calculations (B3LYP/6-311+G**) predict that nucleophilic attack of the aromatic *cyclo*-$Cu_4(\mu\text{-}H)_4$ ring yields ligand-stabilized tetranuclear Cu_4 clusters formulated as *cyclo*-$Cu_4(\mu\text{-}H)_4Nuc_n$ (n = 1-4; Nuc = N_2, CO, H_2O, NH_3 and PH_3). Depending on the number of added nucleophiles, the tetranuclear Cu_4 clusters adopt planar, bent or 3D tetrahedral geometries. These molecules exhibit aromatic character, which is primarily due to 4s and 3d cyclic electron delocalization over the Cu_4 framework (s and d-orbital aromaticity). The aromaticity of the novel ligand stabilized tetranuclear Cu_4 clusters was verified by a number of established criteria of aromaticity. In particular, the nucleus-independent chemical shift, NICS(0) and NICS(1) and their out-of-plane components $NICS_{zz}(0)$, $NICS_{zz}(1)$ and the NICS scan pictures are indicative for the aromaticity of the planar, bent and tetrahedral Cu_4 clusters. The effect of the substituents on the aromatic character of the Cu_4 clusters is also a main concern of the present work. It was found that increasing the number of the attacking nucleophiles increases the diatropic response of the aromatic tetranuclear Cu_4 clusters. Moreover, the aromaticity of the 3D structures (spherical aromaticity) is higher than the aromaticity of the planar and bent structures. The effect of the coordinated nucleophiles, Nuc, on the stability, geometry, electronic structure and bonding mode of the *cyclo*-$Cu_4(\mu\text{-}H)_4Nuc_n$ molecules is also thoroughly discussed.

Keywords: Aromaticity, DFT calculations, Four-member copper rings, nucleophilic attack, metallaromaticity.

1. INTRODUCTION

Recently, we have communicated on a new class of cyclic copper(I) hydrides (hydrocoppers) formulated as $Cu_n(\mu\text{-}H)_n$ (n = 3-6) as the cyclic hydrocarbon analogues in the diverse tapestry of inorganic chemistry [1]. The choice of the copper(I) hydrides was based on the well known tendency of copper(I) centers to cluster together in a variety of organo-copper(I) compounds involving even the alkyl groups as bridging ligands, a representative example being the cyclic Cu_4R_4 tetramer [2-11]. The cyclic hydrocoppers(I) and some of their substituted derivatives were predicted to be stable species with a perfectly planar configuration, thus expanding the borders of inorganic chemistry into the realm of organic chemistry by building molecules containing bonds that are characterized by a common ring-shaped electron density, more commonly seen in organic molecules, with new properties and chemical reactivity. Moreover, these findings may not only expand the aromaticity concept in all-metal systems with structures resembling those of the aromatic hydrocarbons, but may also indicate whole classes of new inorganic aromatic species (substituted derivatives) resulting upon substitution of the H atoms by other groups such as alkyls (R) and aryls (Ar), halides (X), amido (NR_2), hydroxide (OH) and alkoxides (OR) etc.

The structures of $HCN\text{-}Cu_n$ (n = 1-3) clusters were determined through high resolution infrared spectroscopy [12]. All complexes were found to be bound to the nitrogen end of the HCN molecule and on the "atop site" of the copper cluster. The HCN-Cu interactions changes from a strong van der Waals bond in n = 1 to a partially covalent bond in $HCN\text{-}Cu_3$. Very recently [13] the important intermediate phenyl-copper complexes $[C_6H_5Cu_m]^-$ (m = 1-3), which are produced from the reactions between copper metal clusters formed by laser ablation and the benzene molecules seeded in argon carrier gas, were studied by photoelectron spectroscopy (PES) and density functional theory (DFT).

Herein we address a number of important issues related to the response of the aromatic *cyclo*-$Cu_4(\mu\text{-}H)_4$ molecule towards successive nucleophilic attack by a series of nucleophiles, Nuc, yielding ligand-stabilized tetranuclear Cu_4 clusters formulated as *cyclo*-$Cu_4(\mu\text{-}H)_4Nuc_n$ (n = 1-4; Nuc = N_2, CO, H_2O, NH_3 and PH_3). The molecular and electronic structures, stabilities and bonding features of these novel ligand-stabilized tetranuclear Cu_4 clusters are thoroughly presented, using electronic structure calculation methods at the DFT level of theory.

2. THEORETICAL METHODS

In view of the good performance of density functional theory (DFT), we were instigated to perform DFT calculations at the B3LYP level of theory on all of the compounds we studied using the GAUSSIAN03 program suite [14]. The geometries of all species were fully optimized at the Becke's 3-Parameter hybrid functional [15,16] combined with the Lee-Yang-Parr [17] correlation functional abbreviated as B3LYP level of density functional theory, using the 6-311+G(d,p) basis set. Full geometry optimization was performed for each structure using Schlegel's analytical gradient method [18], and the attainment of the energy minimum

*Address correspondence to this author at the Laboratory of Applied Quantum Chemistry, Faculty of Chemistry, Aristotle University of Thessaloniki, 541 24 Thessaloniki, Greece; E-mail: tsipis@chem.auth.gr

was verified by calculating the vibrational frequencies that result in absence of imaginary eigenvalues. The vibrational modes and the corresponding frequencies are based on a harmonic force field. This was achieved with the SCF convergence on the density matrix of at least 10^{-9} and the rms force less than 10^{-4} au. All bond lengths and bond angles were optimized to better than 0.001 Å and 0.1°, respectively. The computed electronic energies were corrected to constant pressure and 298 K, for zero point energy (ZPE) differences and for the contributions of the translational, rotational and vibrational partition functions. Magnetic shielding tensors have been computed with the GIAO (gauge-including atomic orbitals) DFT method [19] as implemented in the GAUSSIAN03 series of programs [14] employing the B3LYP level of theory. Nucleus-Independent Chemical Shifts (NICS) values were computed at the B3LYP/6-311+G(d,p) level according to the procedure described by Schleyer *et al.* [20]. The magnetic shielding tensor elements was calculated for a ghost atom located at the center of the ring. Negative (diatropic) NICS values indicate aromaticity, while positive (paratropic) values imply antiaromaticity.

3. RESULTS AND DISCUSSION

3.1. Structures of the *cyclo*-Cu$_4$(μ-H)$_4$Nuc$_n$ (n = 1-4; Nuc = N$_2$, CO, H$_2$O, NH$_3$ and PH$_3$) Molecules

Stationary point geometries of the *cyclo*-Cu$_4$(μ-H)$_4$Nuc$_n$ (n = 1-4; Nuc = N$_2$, CO, H$_2$O, NH$_3$ and PH$_3$) molecules computed at the B3LYP/6-311+G(d,p) level of theory are presented in Figs. (**1**) and (**2**).

Perusal of Figs. (**1**) and (**2**) reveals that the addition of the nucleophiles, Nuc (Nuc = N$_2$, CO, H$_2$O, NH$_3$ and PH$_3$) to the Cu(I) metal centers of the parent *cyclo*-Cu$_4$(μ-H)$_4$ (D_{4h}) molecule in some cases alters the planar *cyclo*-Cu$_4$(μ-H)$_4$ stereochemistry affording three-dimensional (3D) structures with C_{2v}, C_{3v} and T_d symmetries. In the case of the addition of two carbonyl ligands in 1,2-positions of the ring, ring opening occurs by insertion of the hydride ligand between the two copper atoms bearing the carbonyl ligands, yielding complex **7**. The addition of one and two nucleophiles, Nuc, changes the rectangular Cu$_4$ core structure (D_{4h} point group) of the parent molecule to a rhombic core structure having C_{2v} and D_{2h} symmetry, respectively.

Nucleophilic attack of the *cyclo*-Cu$_4$(μ-H)$_4$ species by one and two N$_2$ nucleophiles does not alter the planarity of the *cyclo*-Cu$_4$(μ-H)$_4$ cluster, yielding the *cyclo*-Cu$_4$(μ_2-H)$_4$(η^1-N$_2$), **1** and *cyclo*-Cu$_4$(μ_2-H)$_4$(η^1-N$_2$)$_2$, **2**, complexes, having C_{2v} and D_{2h} symmetry, respectively. Dinitrogen is coordinated to copper(I) centers in an end-on coordination mode (η^1-N$_2$). Moreover, in complex **2** the distance between the copper atoms, which have not attacked by the nucleophile, is 2.855 Å, indicating weak intermetallic interactions between these two copper atoms as well. On the other hand, nucleophilic attack of the *cyclo*-Cu$_4$(μ-H)$_4$ species by three and four N$_2$ nucleophiles strongly alters the planarity of the Cu$_4$(μ-H)$_4$ core structure, yielding the 3D structures Cu$_4$(μ_2-H)$_4$(η^1-N$_2$)$_3$, **3** and Cu$_4$(μ_2-H)$_4$(η^1-N$_2$)$_4$, **4**, with C_{3v} and T_d symmetry, respectively. It is important to be noticed that in the 3D structures the hydride ligands are triply-bridged face-capping the tetrahedral structure.

A variety of structures are obtained upon coordination of one to four CO ligands with the copper(I) metal centers of the parent *cyclo*-Cu$_4$(μ-H)$_4$ cluster. Thus, coordination of one CO ligand yields the *cyclo*-Cu$_4$(μ_2-H)$_4$(η^1-CO), **5**, cluster belonging to C_{2v} point group. The addition of the first CO ligand to one of the Cu(I) metal centers results in the shortening of the Cu-Cu bond distance between the non attacked Cu(I) metal centers by 0.021 Å, while the adjacent Cu-Cu bonds are elongated by 0.143 Å with respect to the Cu-Cu bond distance of the parent *cyclo*-Cu$_4$(μ-H)$_4$ molecule (2.440 Å).

Three minima were located on the potential energy surface (PES) of the Cu$_4$H$_4$(CO)$_2$ system. The global minimum corresponds to the planar structure **6** (D_{2h}), with the two CO ligands in 1,3-positions. Noteworthy is the relatively short Cu⋯Cu distance of 2.689 Å between the non attacked Cu(I) centers in the rhombic "all-metal" ring indicating the existence of intermetallic interactions between these copper atoms as well. Conformer **7**, with the two CO ligands in 1,2-positions corresponds to a local minimum 6.9 kcal/mol higher in energy than the global minimum **6**. In conformer **7**, the Cu⋯Cu distance between the copper atoms bearing the CO ligands has dramatically increased to 3.036 Å, illustrating the ring opening at this point and the two copper atoms are only symmetrically bridged by a hydride ligand. The third isomer **8**, corresponding to a local minimum at 27.3 kcal/mol higher in energy than the global minimum, adopts a 3D configuration with C_{2v} symmetry. All bridging hydride ligands are triply bridging ligands face-capping the tetrahedral Cu$_4$(μ_3-H)$_4$(η^1-CO)$_2$ structure. Three minima were also located on the PES of the Cu$_4$H$_4$(CO)$_3$ system. The global minimum, corresponding to conformer **9**, adopts a bent structure of C_s symmetry. The Cu-Cu-Cu-Cu dihedral angle is 147.9°, while the bent around the Cu⋯Cu hinge forms weakly bonding Cu⋯Cu interactions (Cu⋯Cu distance of 2.711 Å). Conformer **10**, adopting a 3D tetrahedral structure of C_{3v} symmetry, corresponds to a local minimum 9.6 kcal/mol higher in energy with respect to the global minimum **9**. The planar conformer **11** belonging to C_{2v} point group corresponds to a saddle point ($v = 35.5i$ cm^{-1}), 2.2 kcal/mol higher in energy with respect to the global minimum. Following the imaginary frequency and re-optimizing the structure the global minimum is achieved. Finally, for the Cu$_4$H$_4$(CO)$_4$ species we were able to locate three minima on the PES corresponding to conformers with tetrahedral, bent and planar structures. In the tetrahedral structure, **12**, with T_d symmetry, corresponding to the global minimum, the Cu-Cu bond distances are 2.536 Å, while all hydride ligands are triply bridging face-capping the tetrahedral structure. The bent structure, **13**, possessing D_{2d} symmetry is a local minimum 7.3 kcal/mol higher in energy. The Cu-Cu-Cu-Cu dihedral angle in **13** is 105.3°. The planar conformer, **14**, of D_{4h} symmetry corresponds to a saddle point ($v = 20.4i$ cm^{-1}) 14.4 kcal/mol higher in energy with respect to the global minimum. Following the imaginary frequency the local minimum, **13**, is obtained.

Analogous is the response of the *cyclo*-Cu$_4$(μ-H)$_4$ species towards the nucleophilic attack by the H$_2$O, NH$_3$ and PH$_3$ nucleophiles (Fig. **2**). Coordination of one and two H$_2$O ligands does not alter the planar configuration of the clusters.
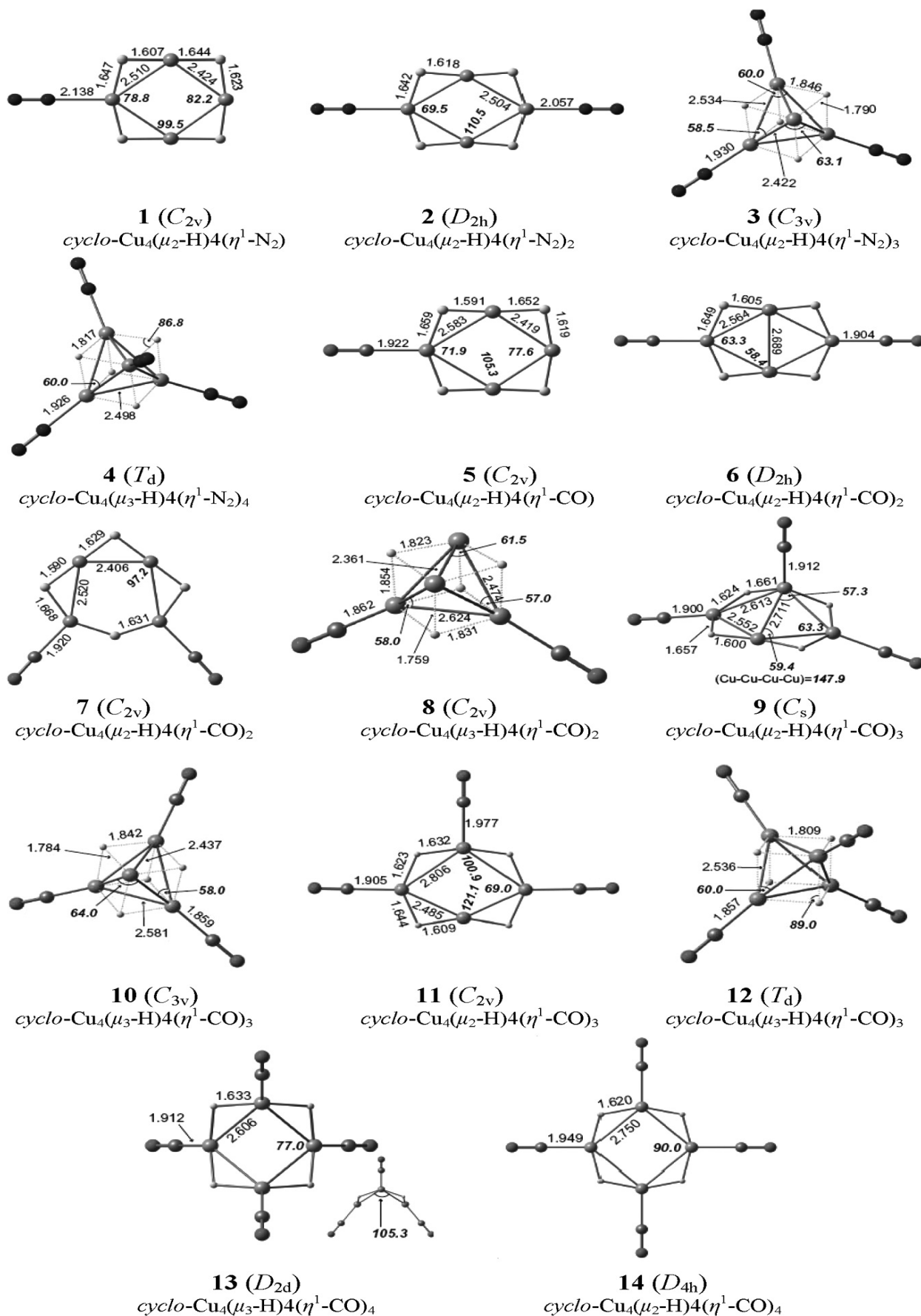
1 (C_{2v})
cyclo-Cu$_4$(μ_2-H)4(η^1-N$_2$)

2 (D_{2h})
cyclo-Cu$_4$(μ_2-H)4(η^1-N$_2$)$_2$

3 (C_{3v})
cyclo-Cu$_4$(μ_2-H)4(η^1-N$_2$)$_3$

4 (T_d)
cyclo-Cu$_4$(μ_3-H)4(η^1-N$_2$)$_4$

5 (C_{2v})
cyclo-Cu$_4$(μ_2-H)4(η^1-CO)

6 (D_{2h})
cyclo-Cu$_4$(μ_2-H)4(η^1-CO)$_2$

7 (C_{2v})
cyclo-Cu$_4$(μ_2-H)4(η^1-CO)$_2$

8 (C_{2v})
cyclo-Cu$_4$(μ_3-H)4(η^1-CO)$_2$

9 (C_s)
cyclo-Cu$_4$(μ_2-H)4(η^1-CO)$_3$

10 (C_{3v})
cyclo-Cu$_4$(μ_3-H)4(η^1-CO)$_3$

11 (C_{2v})
cyclo-Cu$_4$(μ_2-H)4(η^1-CO)$_3$

12 (T_d)
cyclo-Cu$_4$(μ_3-H)4(η^1-CO)$_3$

13 (D_{2d})
cyclo-Cu$_4$(μ_3-H)4(η^1-CO)$_4$

14 (D_{4h})
cyclo-Cu$_4$(μ_2-H)4(η^1-CO)$_4$

Fig. (1). Equilibrium geometries (bond lengths in Angstroms, angles in deg) of the stationary points located on the PES of the Cu$_4$(l-H)$_4$Nuc$n$ (n = 1-4; Nuc = N$_2$, CO) molecules, computed at the B3LYP/6-311+G(d,p) level.

15 (C_s)

cyclo-Cu$_4$(μ_2-H)$_4$(OH$_2$)

16 (C_{2h})

cyclo-Cu$_4$(μ_2-H)$_4$(OH$_2$)$_2$

17 (C_s)

cyclo-Cu$_4$(μ_2-H)$_4$(OH$_2$)$_3$

18 (C_s)

cyclo-Cu$_4$(μ_2-H)$_2$(μ_3-H)$_2$(NH$_3$)

19 (C_{2h})

cyclo-Cu$_4$(μ_2-H)$_4$(NH$_3$)$_2$

20 (T_d)

cyclo-Cu$_4$(μ_3-H)$_4$(NH$_3$)$_4$

21 (C_s)

cyclo-Cu$_4$(μ_3-H)$_4$(PH$_3$)

22 (C_{2h})

cyclo-Cu$_4$(μ_2-H)$_4$(PH$_3$)$_2$

23 (C_s)

cyclo-Cu$_4$(μ_2-H)$_4$(PH$_3$)$_2$

24 (C_{3v})

cyclo-Cu$_4$(μ_3-H)$_4$(PH$_3$)$_3$

25 (D_{2d})

cyclo-Cu$_4$(μ_2-H)$_4$(PH$_3$)$_4$

26 (T_d)
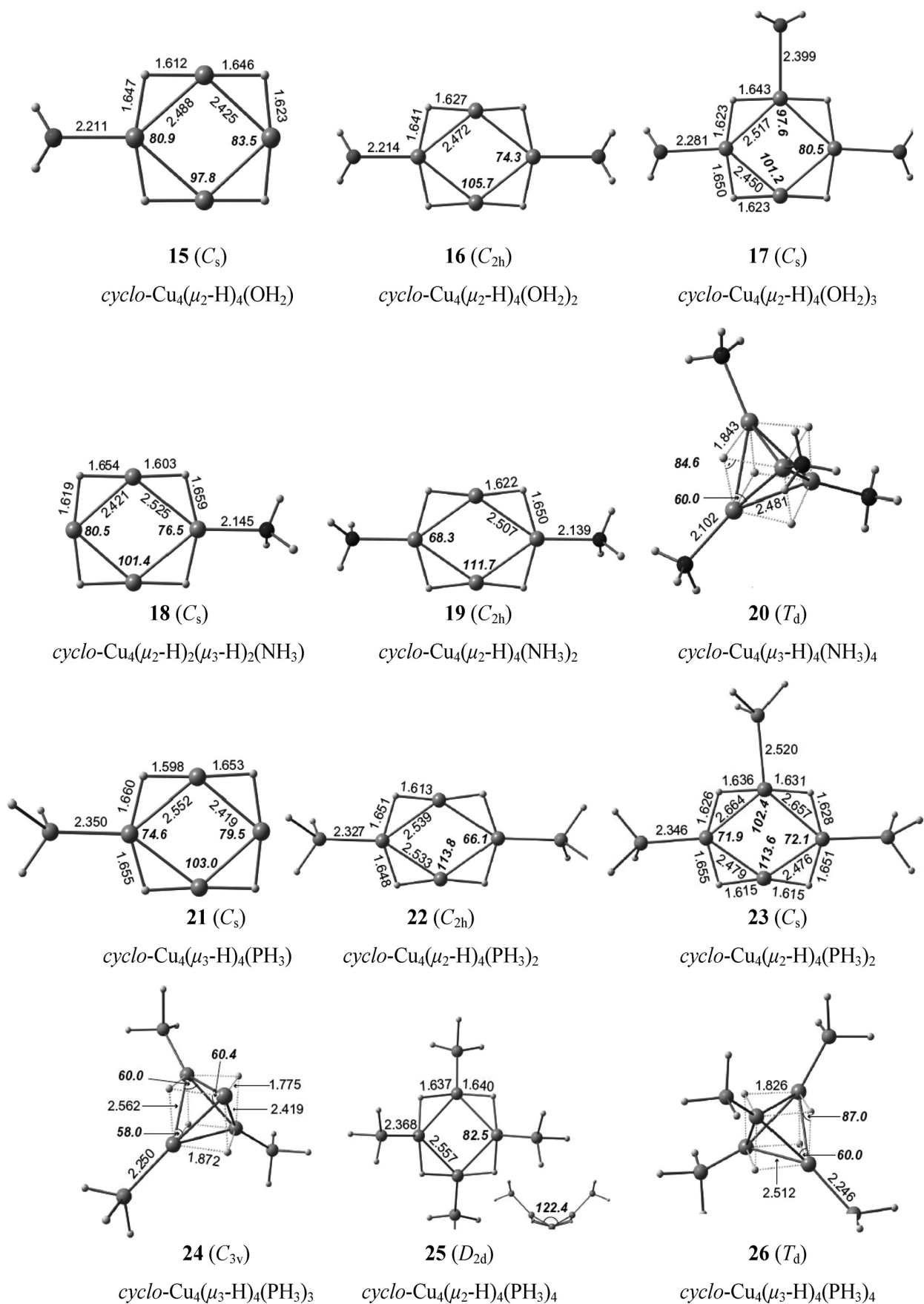
cyclo-Cu$_4$(μ_3-H)$_4$(PH$_3$)$_4$

Fig. (2). Equilibrium geometries (bond lengths in Angstroms, angles in deg) of the stationary points located on the PES of the Cu$_4$($\ddot{l}$-H)4Nuc$_n$ (n = 1-4; Nuc = OH$_2$, NH$_3$, PH$_3$) molecules, computed at the B3LYP/6-311+G(d,p) level.

In the $cyclo\text{-}Cu_4(\mu\text{-}H)_4(OH_2)$, **15**, cluster the hydrogen atoms of the coordinated H_2O molecule are oriented out of the molecular plane, thereby the symmetry of the molecule is the C_s. The same holds also true for the $cyclo\text{-}Cu_4(\mu\text{-}H)_4(OH_2)_2$ species, **16** of C_{2h} symmetry where the hydrogen atoms of the coordinated H_2O molecules are oriented on both sides of the molecular plane. Another conformer of C_{2v} symmetry with the hydrogen atoms of the coordinated H_2O molecules oriented on one side of the molecular plane corresponds to a local minimum 0.04 kcal/mol higher in energy than the global minimum, **16**. Notice that only the $cyclo\text{-}Cu_4(\mu\text{-}H)_4(OH_2)_2$ conformers with the coordinated H_2O molecules in 1,3-positions were located in the PES. The global minimum of the $Cu_4H_4(OH_2)_3$ system corresponds to the planar structure **17** (C_s), while a 3D tetrahedral structure, **18** (C_3) is a local minimum at 26.4 kcal/mol higher in energy. Attempts to locate a minimum in the PES of the $Cu_4H_4(OH_2)_4$ system were unsuccessful.

Nucleophilic attack of the $cyclo\text{-}Cu_4(\mu\text{-}H)_4$ species by one molecule of the NH_3 nucleophile, affords the $cyclo\text{-}Cu_4(\mu\text{-}H)_4(NH_3)$, **19**, cluster, which keeps the planarity of the parent $cyclo\text{-}Cu_4(\mu\text{-}H)_4$ molecule. Notice that one of the hydrogen atoms of the coordinated NH_3 ligand is coplanar with the molecular plane. The second NH_3 ligand is coordinated to a Cu(I) center in 1,3-positions affording the $cyclo\text{-}Cu_4(\mu\text{-}H)_4(NH_3)_2$, **20**, cluster having C_{2h} symmetry. Attempts to locate a minimum in the PES of the $Cu_4H_4(NH_3)_3$ system were unsuccessful. The fully substituted $Cu_4(\mu\text{-}H)_4(NH_3)_4$, **21**, cluster adopts a 3D tetrahedral stereochemistry belonging to T_d point group. In the T_d structure all bridging hydride ligands are triply bridging face-capping the tetrahedron.

Finally, the successive nucleophilic attack of the aromatic parent $cyclo\text{-}Cu_4(\mu\text{-}H)_4$ molecule by the PH_3 nucleophile yields mono-, di-, tri- and tetra-substituted derivatives. The mono-substituted derivative, **22**, retains the planarity of the parent $cyclo\text{-}Cu_4(\mu\text{-}H)_4$ species, but the perfect square planar Cu_4 core of the parent molecule is transformed to a rhombic "all-metal" core. In the di-substituted derivative, **23**, of C_{2h} symmetry, the two PH_3 ligands occupy the 1,3-positions in the rhombic Cu_4 structural core. Two tri-substituted derivatives were located on the PES of the $Cu_4H_4(PH_3)_3$ system. The global minimum corresponds to a planar structure, **24**, having C_s symmetry, while a 3D structure, **25**, of C_{3v} symmetry is a local minimum 14.9 kcal/mol higher in energy. For the tetra-substituted $cyclo\text{-}Cu_4(\mu\text{-}H)_4(PH_3)_4$ derivative the global minimum corresponds to the bent structure, **26**, belonging to D_{2d} point group, while the 3D structure, **27**, with T_d symmetry is a local minimum only 1.7 kcal/mol higher in energy. Notice again the triply bridging hydride ligands face-capping the tetrahedron.

3.2. Stability of the $cyclo\text{-}Cu_4(\mu\text{-}H)_4L_n$ (n = 1-4; Nuc = N_2, CO, H_2O, NH_3 and PH_3) Molecules

The stability of the $cyclo\text{-}Cu_4(\mu\text{-}H)_4Nuc_n$ (n = 1-4; Nuc = N_2, CO, H_2O, NH_3 and PH_3) molecules are investigated using the following fragmentation pattern:

$$cyclo\text{-}Cu_4(\mu\text{-}H)_4Nuc_n \rightarrow cyclo\text{-}Cu_4(\mu\text{-}H)_4 + nNuc$$
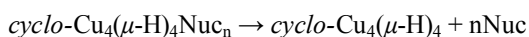
The calculated binding energies are compiled in Table **1**.

Table 1. Total Electronic Energy E (in Hartrees) and Binding Energies ΔE_1, ΔE_2 and ΔE_3 (in kcal/mol) of the $cyclo\text{-}Cu_4(\mu\text{-}H)_4Nuc_n$ (n = 1-4; Nuc = N_2, CO, H_2O, NH_3 and PH_3) Molecules Computed at the B3LYP/6-311+G(d,p) Level

Cluster	Point Group	ΔE_1[a] [kcal/mol]	$\Delta E_1/n$ [kcal/mol]
$cyclo\text{-}Cu_4(\mu\text{-}H)_4(N_2)$, **1**	C_{2v}	-0.8	-0.8
$cyclo\text{-}Cu_4(\mu\text{-}H)_4(N_2)_2$, **2**	D_{2h}	-2.3	-1.2
$Cu_4(\mu\text{-}H)_4(N_2)_3$, **3**	C_{3v}	-25.1	-8.4
$Cu_4(\mu\text{-}H)_4(N_2)_4$, **4**	T_d	-33.7	-8.4
$cyclo\text{-}Cu_4(\mu\text{-}H)_4(CO)$, **5**	C_{2v}	-10.2	-10.2
$cyclo\text{-}Cu_4(\mu\text{-}H)_4(CO)_2$, **6**	D_{2h}	-23.6	-11.8
$cyclo\text{-}Cu_4(\mu\text{-}H)_4(CO)_2$, **7**	C_{2v}	-16.8	-8.4
$Cu_4(\mu\text{-}H)_4(CO)_2$, **8**	C_{2v}	-42.8	-21.4
$cyclo\text{-}Cu_4(\mu\text{-}H)_4(CO)_3$, **9**	C_s	-28.0	-9.3
$Cu_4(\mu\text{-}H)_4(CO)_3$, **10**	C_{3v}	-64.9	-21.6
$cyclo\text{-}Cu_4(\mu\text{-}H)_4(CO)_3$, **11**	C_{2v}	-25.8	-8.6
$Cu_4(\mu\text{-}H)_4(CO)_4$, **12**	T_d	-87.2	-21.8
$cyclo\text{-}Cu_4(\mu\text{-}H)_4(CO)_4$, **13**	D_{2d}	-33.4	-8.3
$cyclo\text{-}Cu_4(\mu\text{-}H)_4(CO)_4$, **14**	D_{2h}	-26.3	-6.6
$cyclo\text{-}Cu_4(\mu\text{-}H)_4(OH_2)$, **15**	C_s	-6.1	-6.1
$cyclo\text{-}Cu_4(\mu\text{-}H)_4(OH_2)_2$, **16**	C_{2h}	-11.5	-5.8
$cyclo\text{-}Cu_4(\mu\text{-}H)_4(OH_2)_3$, **17**	C_s	-12.4	-4.1
$Cu_4(\mu\text{-}H)_4(OH_2)_3$, **18**	C_3	-32.5	-10.8
$cyclo\text{-}Cu_4(\mu\text{-}H)_4(NH_3)$, **19**	C_s	-11.7	-11.7
$cyclo\text{-}Cu_4(\mu\text{-}H)_4(NH_3)_2$, **20**	C_{2h}	-22.8	-11.4
$Cu_4(\mu\text{-}H)_4(NH_3)_4$, **21**	T_d	-58.5	-14.6
$cyclo\text{-}Cu_4(\mu\text{-}H)_4(PH_3)$, **22**	C_s	-9.0	-9.0
$cyclo\text{-}Cu_4(\mu\text{-}H)_4(PH_3)_2$, **23**	C_{2h}	-19.1	-9.6
$cyclo\text{-}Cu_4(\mu\text{-}H)_4(PH_3)_3$, **24**	C_s	-19.7	-6.6
$Cu_4(\mu\text{-}H)_4(PH_3)_3$, **25**	C_{3v}	-51.2	-17.1
$cyclo\text{-}Cu_4(\mu\text{-}H)_4(PH_3)_4$, **26**	D_{2d}	-22.0	-5.5
$Cu_4(\mu\text{-}H)_4(PH_3)_4$, **27**	T_d	-66.8	-16.7

Footnotes: a). $\Delta E_1 = E(cyclo\text{-}Cu_4(\mu\text{-}H)_4Nuc_n) - \{E[cyclo\text{-}Cu_4(\mu\text{-}H)_4] + nE(Nuc)\}$.

It can be seen that all nucleophiles, Nuc, are loosely associated with the parent $cyclo\text{-}Cu_4(\mu\text{-}H)_4$ molecule, the estimated interaction energies were found in the range of -0.8 to -21.8 kcal/mol. In particular, dinitrogen, N_2, is the most loosely coordinated ligand with the Cu(I) centers, with interaction energies in the range of -0.8 to -8.4 kcal/mol. On the other hand, carbonyl, CO, forms stronger Cu-CO coordination bonds with bond energies in the range of -6.6 to -21.8 kcal/mol. The estimated $Cu\text{-}OH_2$, $Cu\text{-}NH_3$ and $Cu\text{-}PH_3$ bond energies were found in the ranges of -4.1 to -6.1, -11.4 to -14.6 and -5.5 to -17.1 kcal/mol, respectively. All nucleo-

Table 2. **The Hardness, η, and the Electrophilicity Index, ω, of the *cyclo*-Cu$_4$(μ-H)$_4$Nuc$_n$ (n = 1-4; Nuc = N$_2$, CO, H$_2$O, NH$_3$ and PH$_3$) Clusters Computed at the B3LYP/6-311+G(d,p) Level**

Cluster	η [eV]	ω [eV]
cyclo-Cu$_4$(μ-H)$_4$(N$_2$), **1**	2.15	2.12
cyclo-Cu$_4$(μ-H)$_4$(N$_2$)$_2$, **2**	1.98	2.16
Cu$_4$(μ-H)$_4$(N$_2$)$_3$, **3**	1.93	1.95
Cu$_4$(μ-H)$_4$(N$_2$)$_4$, **4**	1.96	2.00
cyclo-Cu$_4$(μ-H)$_4$(CO), **5**	1.98	2.47
cyclo-Cu$_4$(μ-H)$_4$(CO)$_2$, **6**	1.85	2.52
cyclo-Cu$_4$(μ-H)$_4$(CO)$_2$, **7**	1.92	2.52
Cu$_4$(μ-H)$_4$(CO)$_2$, **8**	1.94	2.08
cyclo-Cu$_4$(μ-H)$_4$(CO)$_3$, **9**	2.04	2.39
Cu$_4$(μ-H)$_4$(CO)$_3$, **10**	1.96	2.19
cyclo-Cu$_4$(μ-H)$_4$(CO)$_3$, **11**	1.72	2.59
Cu$_4$(μ-H)$_4$(CO)$_4$, **12**	2.02	2.36
cyclo-Cu$_4$(μ-H)$_4$(CO)$_4$, **13**	2.03	2.47
cyclo-Cu$_4$(μ-H)$_4$(CO)$_4$, **14**	1.78	2.46
cyclo-Cu$_4$(μ-H)$_4$(OH$_2$), **15**	2.41	1.41
cyclo-Cu$_4$(μ-H)$_4$(OH$_2$)$_2$, **16**	2.24	1.22
cyclo-Cu$_4$(μ-H)$_4$(OH$_2$)$_3$, **17**	2.13	1.07
Cu$_4$(μ-H)$_4$(OH$_2$)$_3$, **18**	1.73	1.19
cyclo-Cu$_4$(μ-H)$_4$(NH$_3$), **19**	2.36	1.29
cyclo-Cu$_4$(μ-H)$_4$(NH$_3$)$_2$, **20**	2.15	1.04
Cu$_4$(μ-H)$_4$(NH$_3$)$_4$, **21**	1.44	0.68
cyclo-Cu$_4$(μ-H)$_4$(PH$_3$), **22**	2.34	1.53
cyclo-Cu$_4$(μ-H)$_4$(PH$_3$)$_2$, **23**	2.15	1.36
cyclo-Cu$_4$(μ-H)$_4$(PH$_3$)$_3$, **24**	1.95	1.22
Cu$_4$(μ-H)$_4$(PH$_3$)$_3$, **25**	2.11	0.92
cyclo-Cu$_4$(μ-H)$_4$(PH$_3$)$_4$, **26**	2.09	1.04
Cu$_4$(μ-H)$_4$(PH$_3$)$_4$, **27**	2.12	0.84

Table 3. **The NICS Values (in ppm) Calculated at the Ring Center, NICS(0), 1.0 Å Above the Ring Center, NICS(1) and the Corresponding zz-Components NICS$_{zz}$(0) and NICS$_{zz}$(1) of the Shielding Tensor Element, for the *cyclo*-Cu$_4$(μ-H)$_4$Nuc$_n$ (n = 1-4; Nuc = N$_2$, CO, H$_2$O, NH$_3$ and PH$_3$) Molecules Computed at the GIAO/ B3LYP/6-311+G(d,p) Level**

Cluster	NICS(0)	NICS(1)	NICS$_{zz}$(0)	NICS$_{zz}$(1)
cyclo-Cu$_4$(μ-H)$_4$(N$_2$), **1**	-6.9	-3.1	12.5	-0.5
cyclo-Cu$_4$(μ-H)$_4$(N$_2$)$_2$, **2**	-7.6	-5.5	14.9	-0.1
Cu$_4$(μ-H)$_4$(N$_2$)$_3$, **3**	-22.7	-	-	-
Cu$_4$(μ-H)$_4$(N$_2$)$_4$, **4**	-21.2	-	-	-
cyclo-Cu$_4$(μ-H)$_4$(CO), **5**	-9.3	-4.1	10.1	-2.2
cyclo-Cu$_4$(μ-H)$_4$(CO)$_2$, **6**	-8.6	-3.3	15.5	-1.3
cyclo-Cu$_4$(μ-H)$_4$(CO)$_2$, **7**	-8.6	-3.9	5.5	-2.3
Cu$_4$(μ-H)$_4$(CO)$_2$, **8**	-22.4	-	-	-
cyclo-Cu$_4$(μ-H)$_4$(CO)$_3$, **9**	-9.9	-	-	-
Cu$_4$(μ-H)$_4$(CO)$_3$, **10**	-19.7	-	-	-
cyclo-Cu$_4$(μ-H)$_4$(CO)$_3$, **11**	-	-	-	-
Cu$_4$(μ-H)$_4$(CO)$_4$, **12**	-17.4	-	-	
cyclo-Cu$_4$(μ-H)$_4$(CO)$_4$, **13**	-10.7	-	-	-
cyclo-Cu$_4$(μ-H)$_4$(CO)$_4$, **14**	-	-	-	-
cyclo-Cu$_4$(μ-H)$_4$(OH$_2$), **15**	-6.9	-3.1	12.2	-0.7
cyclo-Cu$_4$(μ-H)$_4$(OH$_2$)$_2$, **16**	-7.0	-2.9	14.3	-0.1
cyclo-Cu$_4$(μ-H)$_4$(OH$_2$)$_3$, **17**	-6.9	-3.2	12.6	-0.3
Cu$_4$(μ-H)$_4$(OH$_2$)$_3$, **18**	-16.0	-	-	-
cyclo-Cu$_4$(μ-H)$_4$(NH$_3$), **19**	-7.0	-3.1	12.3	-0.8
cyclo-Cu$_4$(μ-H)$_4$(NH$_3$)$_2$, **20**	-7.2	-2.7	16.2	0.1
Cu$_4$(μ-H)$_4$(NH$_3$)$_4$, **21**	-20.7	-	-	-
cyclo-Cu$_4$(μ-H)$_4$(PH$_3$), **22**	-6.8	-3.0	13.0	-0.5
cyclo-Cu$_4$(μ-H)$_4$(PH$_3$)$_2$, **23**	-7.1	-2.7	16.9	0.2
cyclo-Cu$_4$(μ-H)$_4$(PH$_3$)$_3$, **24**	-6.7	-3.0	13.2	-0.2
Cu$_4$(μ-H)$_4$(PH$_3$)$_3$, **25**	-17.8	-	-	-
cyclo-Cu$_4$(μ-H)$_4$(PH$_3$)$_4$, **26**	-8.0	-3.9	10.5	2.6
Cu$_4$(μ-H)$_4$(PH$_3$)$_4$, **27**	-14.5	-	-	-

philes are more strongly bonded in the 3D than the planar or bent structures. Moreover, the bond energies increase upon increasing the number of the coordinated nucleophiles.

We have also computed the heat of formation of the *cyclo*-Cu$_4$(μ-H)$_4$Nuc$_4$ molecules upon tetramerization of their HCuL monomeric species according to the chemical equation:

$$4HCuNuc \rightarrow cyclo\text{-}Cu_4(\mu\text{-}H)_4Nuc_4$$

It was found that all formation processes are exothermic indicating that these species could be isolated in their cyclic tetrameric form within a supersonic jet. The estimated formation energies were found to be -76.3, -85.9, -45.1 and -77.1 kcal/mol for the Cu$_4$(μ-H)$_4$(N$_2$)$_4$, Cu$_4$(μ-H)$_4$(CO)$_4$,

Cu$_4$(μ-H)$_4$(NH$_3$)$_4$ and Cu$_4$(μ-H)$_4$(PH$_3$)$_4$ complexes, respectively. It is worth to be noticed that fully substituted complexes involving the OH$_2$ nucleophile was not possible to be located on the PES either as local minima or saddle points.

3.3. The Hardness and Electrophilicity of the *cyclo*-Cu$_4$(μ-H)$_4$Nuc$_n$ (n = 1-4; Nuc = N$_2$, CO, H$_2$O, NH$_3$ and PH$_3$) Molecules

The hardness and electrophilicity parameters of the *cyclo*-Cu$_4$(μ-H)$_4$Nuc$_n$ (n = 1-4; L = N$_2$, CO, H$_2$O, NH$_3$ and PH$_3$) molecules are compiled in Table **2**.
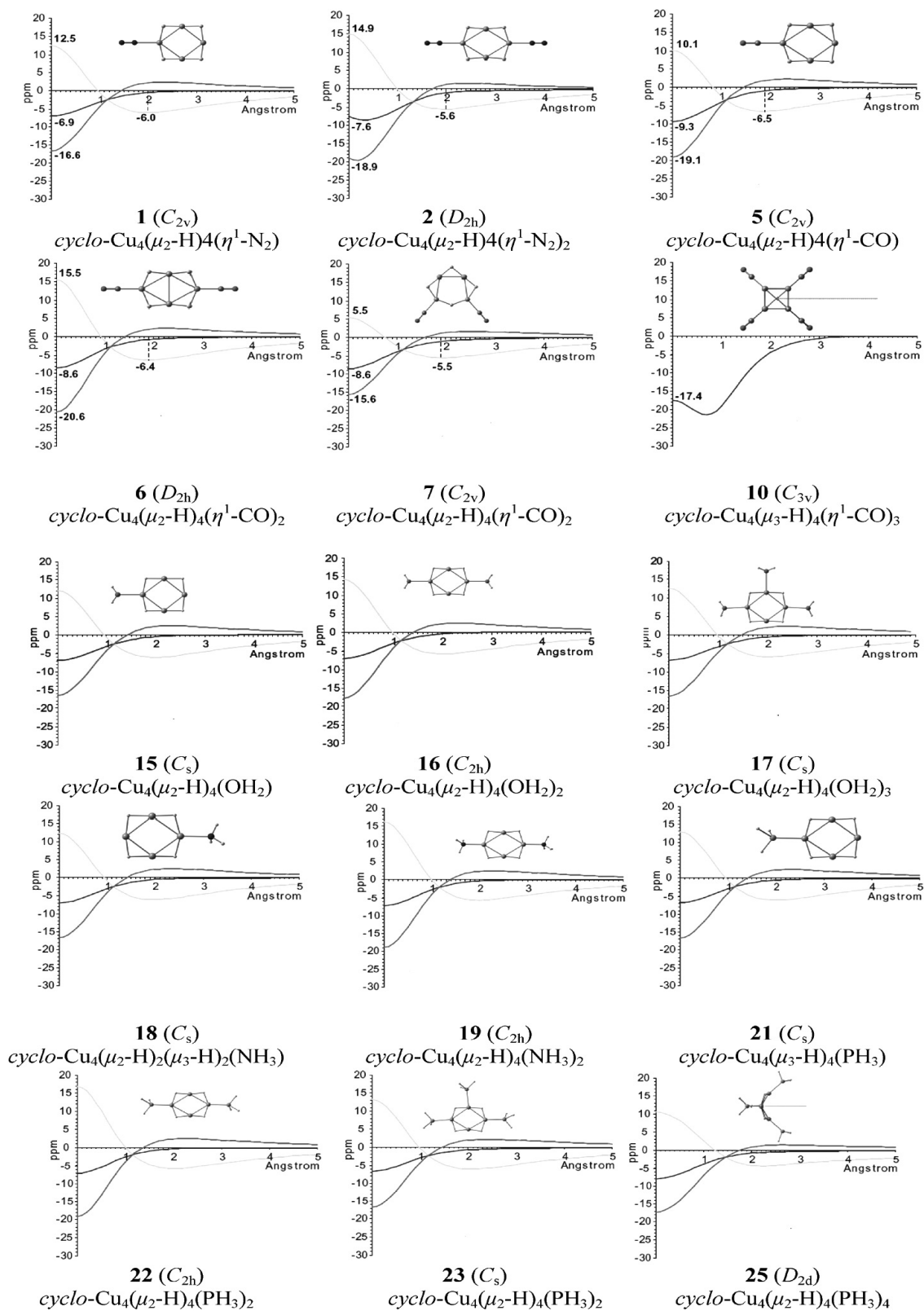
Fig. (3). The NICS scan pictures for the isotropic σ^{iso}(bq) ———, σ^{zz}(bq$_{out}$) ———, and σ (bq$_{in}$) ——— tensors of representative *cyclo*-Cu$_4$(μ-H)$_4$Nuc$_n$ (n = 1-4; Nuc = N$_2$, CO, OH$_2$, NH$_3$, PH$_3$) molecules computed at the B3LYP/6-311+G(d,p) level.

The high stability of the *cyclo*-Cu$_4$(μ-H)$_4$L$_n$ (n = 1-4; L = N$_2$, CO, H$_2$O, NH$_3$ and PH$_3$) molecules is also reflected on the estimated high values of hardness, η defined as $\eta = (\varepsilon_{LUMO} - \varepsilon_{HOMO})/2$ [21]. Generally, according to the com-

puted η values the stability of the *cyclo*-Cu$_4$(μ-H)$_4$L$_n$ molecules decreases upon increasing the degree of substitution. According to the hardness, the stability of the *cyclo*-Cu$_4$(μ-

H)$_4$L$_n$ molecules follows the trend: H$_2$O > NH$_3$ > PH$_3$ > N$_2$ > CO.

The electrophilicity index ω (Table **2**) computed [22] as $\omega = \mu^2/2\eta$, where μ and η are the chemical potential and hardness respectively, given approximately by the expressions $\mu = (\varepsilon_{LUMO} + \varepsilon_{HOMO})/2$ and $\eta = (\varepsilon_{LUMO} - \varepsilon_{HOMO})$ measures the electrophilic character of the four-member ring and consequently is a measure of the aromatic character of the ring. It can be seen that the electrophilicity decreases upon increasing substitution. The electrophilicity of the four-member ring core structure follows the trend: CO > N$_2$ >PH$_3$ > H$_2$O > NH$_3$. The lowering of the electrophilicity of the *cyclo*-Cu$_4$(μ-H)$_4$(OH$_2$)$_{1-4}$ and *cyclo*-Cu$_4$(μ-H)$_4$(NH$_3$)$_{1-4}$ species involving the pure σ-donor H$_2$O and NH$_3$ ligands could be attributed to the increase of the π-electron density on the four-membered Cu$_4$ ring.

3.4. Aromacity/Antiaromaticity of the *cyclo*-Cu$_4$(μ-H)$_4$ Nuc$_n$ (n = 1-4; Nuc = N$_2$, CO, H$_2$O, NH$_3$ and PH$_3$) Molecules

Planarity, high stability, bond length equalization and hardness are conventionally good indicators of aromaticity, but this is restrictive in many examples. In order to quantify the aromaticity/antiaromaticity of the clusters we applied the magnetic criterion, viz. nucleus-independent chemical shift (NICS), proposed by Schleyer *et al.* [20]. Negative (diatropic) NICS values indicate aromaticity, while positive (paratropic) values imply antiaromaticity. NICS(0) is usually computed at the ring centers, but also can be calculated at certain distance above or below the center of the ring; the NICS obtained at 1 Å above the ring centroid, NICS(1) as well as the NICS$_{zz}$(1) tensor component are considered to be better aromaticity indices than NICS(0) [23,24]. The NICS(0), NICS(1), NICS$_{zz}$(0) and NICS$_{zz}$(1) are given in Table **3**.

To get a better insight into the origin of the aromaticity of the *cyclo*-Cu$_4$(μ-H)$_4$Nuc$_n$ (n = 1-4; Nuc = N$_2$, CO, H$_2$O, NH$_3$ and PH$_3$) molecules we applied the recently proposed NICS scan procedure, which is based on scanning the NICS, σ(bq), values over a distance R and dissecting them into in-plane, σ^{iso}(bq$_{in}$) and out-of-plane, σ^{zz}(bq$_{out}$) components [25,26]. The NICS scan pictures for the isotropic σ^{iso}(bq), σ^{zz}(bq$_{out}$), and σ(bq$_{in}$) tensors of representative molecules are given in Fig. (**3**).

It can be seen that all *cyclo*-Cu$_4$(μ-H)$_4$Nuc$_n$ (n = 1-4; Nuc = N$_2$, CO, H$_2$O, NH$_3$ and PH$_3$) molecules exhibit negative NICS(0) values, only slightly affected by the degree of substitution. On the other hand, the aromaticity of the 3D tetrahedral Cu$_4$ core structures, the so-called spherical aromaticity, is higher than the aromaticity of the isomeric planar structures. Noteworthy is the antiaromaticity of all planar rings suggested by the positive NICS$_{zz}$(0) values. The NICS$_{zz}$(1) values become negative, but very small suggestive of non aromaticity for these systems. However, the NICS$_{zz}$ component acquires negative values (in the range of -5.6 to -10.5 ppm) in a distance of 1.6 – 1.8 Å above the ring plane. Considering that the NICS$_{zz}$ component is a better index of aromaticity [23,24] we could say that all planar structures keep the aromatic character of the parent *cyclo*-Cu$_4$(μ-H)$_4$ molecule.

4. CONCLUSIONS

The results can be summarized as follows:

Successive nucleophilic attack of the parent aromatic *cyclo*-Cu$_4$(μ-H)$_4$ molecule by a series of nucleophiles affords novel *cyclo*-Cu$_4$(μ-H)$_4$Nuc$_n$ (n = 1-4; Nuc = N$_2$, CO, H$_2$O, NH$_3$ and PH$_3$) clusters. Depending on the nature of the nucleophile and the degree of substitution, the *cyclo*-Cu$_4$(μ-H)$_4$Nuc$_n$ clusters adopt planar, bent or 3D tetrahedral geometries. The 3D structures are obtained for the higher degrees of substitution, that is in the Cu$_4$(μ-H)$_4$Nuc$_n$ (n = 3, 4; Nuc = N$_2$, CO, H$_2$O, NH$_3$ and PH$_3$) molecules.

All *cyclo*-Cu$_4$(μ-H)$_4$Nuc$_n$ (n = 1-4; Nuc = N$_2$, CO, H$_2$O, NH$_3$ and PH$_3$) molecules are predicted to be bound with respect to their dissociation according to the following dissociation pattern:

$$cyclo\text{-}Cu_4(\mu\text{-}H)_4Nuc_n \rightarrow cyclo\text{-}Cu_4(\mu\text{-}H)_4 + nNuc$$
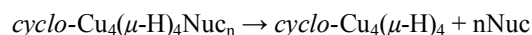
The strength of the M-Nuc association follows the trend: NH$_3$ > CO > PH$_3$ > H$_2$O> N$_2$. The computed bond dissociation energies for the Cu-Nuc bonds span the range of -0.8 to -21.8 kcal/mol.

The bonding of the *cyclo*-Cu$_4$(μ-H)$_4$Nuc$_n$ (n = 1-4; Nuc = N$_2$, CO, H$_2$O, NH$_3$ and PH$_3$) molecules is characterized by a common ring-shaped electron density, which is constructed by highly delocalized σ, π- and δ-type MOs (s and d orbital aromaticity). All *cyclo*-Cu$_4$(μ-H)$_4$Nuc$_n$ molecules in their planar, bent and 3D tetrahedral structures exhibit negative NICS(0) values, and therefore keep the aromatic character of the parent *cyclo*-Cu$_4$(μ-H)$_4$ molecule.

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