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Polynuclear sandwich derivatives of [10]annulene: a quantum chemical study

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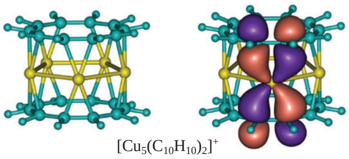
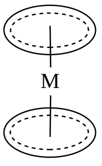
Density-functional theory (DFT) calculations at B3LYP/6-311+G(df,p) and M06/6-311+G(df,p) levels of theory predict the stability of new polynuclear sandwich complexes $[Cu_5(C_{10}H_{10})_2]^+$ and $Ni_5(C_{10}H_{10})_2$ based on flat [10]annulene cycles.



$[Cu_5(C_{10}H_{10})_2]^+$
$Ni_5(C_{10}H_{10})_2$

Keywords: polynuclear sandwich compounds, quantum-chemical calculations, non-standard conformations, [10]annulene, copper complexes, nickel complexes.

Since the discovery of ferrocene,[1,2] sandwich systems **1** have been attracting the attention of both theorists and experimentalists because of their unusual structure, bonding nature, and wide possibilities of technical applications.[3–8] A new direction of research on sandwich systems is the study of polynuclear derivatives, in which a monolayer of several metal atoms is located between hydrocarbon rings.[9–18] Experimentally characterized examples of such systems are palladium complexes, **2**[10] and **3**,[12] with a central ring of three and four metal atoms, respectively. An important aspect of the structure of such compounds is the possibility of stabilizing the non-standard configurations of their basic cyclic fragments. For example, a boat-like cyclooctatetraene ring, C_8H_8, is stabilized in a planar form when it is included into complex **3**.



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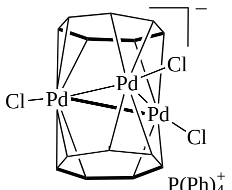

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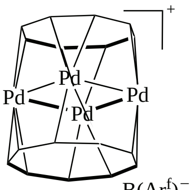
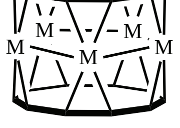


3

Like cyclooctatetraene, cyclodecapentaene $C_{10}H_{10}$ in the free state is characterized by a non-planar structure; however, it can be assumed that its non-standard planar form can be stabilized in polynuclear sandwich complexes. In this paper, we present the first examples of such systems, $[Cu_5(C_{10}H_{10})_2]^+$ and $Ni_5(C_{10}H_{10})_2$ complexes, which include planar [10]annulene basal cycles with a 5-atomic metal layer between them (structure **4**).



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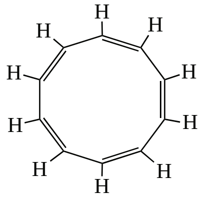
Density functional theory (DFT) calculations were performed with B3LYP[19] and M06[20] functionals and a split valence basis set 6-311+G(df,p)[21] using the Gaussian-16 program package.[22] In previous studies on [10]annulene derivatives,[23–26] B3LYP was shown to be a good choice for describing geometric parameters and vibrational constants, while M06 was chosen here because of its general-purpose applicability.[20] The stationary points on the potential energy surfaces (PESs) were located with full geometry optimizations, identified by calculating the matrix of the second derivatives (force constants) and checked for the stabilities of Hartree–Fock solutions. Natural bond orbital (NBO) analysis[27] was performed with help of the NBO 6.0 program.[28] An atoms-in-molecules (AIM) analysis[29] was carried out using the AIMAll Professional program.[30] The drawings were made using the program suite ChemCraft[31] with calculated atomic coordinates as the input parameters.

According to the calculations at both levels of approximation, the cationic copper sandwich complex **4** (M = Cu) of D_{5h} symmetry corresponds to an energy minimum ($\lambda = 0$, where λ is the number of negative eigenvalues of the second derivatives matrix on the potential energy surface). The annulene fragments are in the eclipsed configuration with respect to each other and in a sterically constrained configuration with respect to the central cyclic Cu_5 fragment. The carbon rings of the annulene fragments are almost planar, while the hydrogen atoms are slightly turned out of the plane.

Although [10]annulene, $C_{10}H_{10}$, has an aromatic 10π-electron system, it is unstable in planar form **5** and in the free state is characterized by a twist (**6a**) and boat-like (**6b**) conformations[32] due to repulsion of destabilizing steric effects of hydrogen atoms that prevail over the effects of aromatic stabilization. Thus, the inclusion of the Cu_5 metallocycle between two $C_{10}H_{10}$ fragments stabilizes the non-standard planar conformation of [10]annulene cycles.

The C–C bonds parameters of the annulene rings in complex **4** (M = Cu) correspond to aromatic ones. The lengths of the bonds involved in the interaction with copper atoms are equal to 1.421 (B3LYP)/1.415 (M06) Å and are slightly reduced compared to the bonds uninvolved in the interaction [1.453



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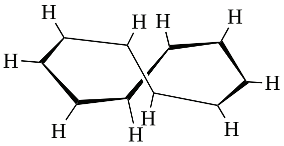
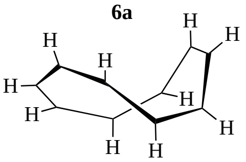


6a

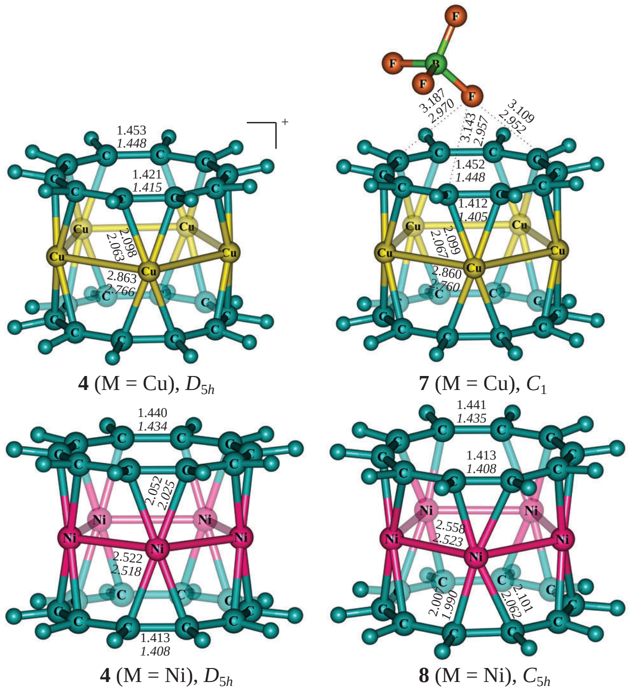


6b

(B3LYP)/1.448 (M06) Å]. The calculated bond lengths between copper atoms are 2.863 (B3LYP)/2.766 (M06) Å, which significantly exceeds the bond length in a Cu_2 dimer (2.2 Å according to experimental data[33]) and is in the range of Cu–Cu bond lengths in various organocopper derivatives (2.35–2.64 Å[34]). In complex **4** (M = Cu), equivalent Cu–C bonds are formed, the lengths of which are 2.098 (B3LYP)/2.063 (M06) Å and are in the range of the parameters of the Cu–C bonds (1.88–2.2 Å) of copper complexes with alkenes.[35] The presence of multiple Cu–C bonds ensures the formation of a rigid framework of the complex and contributes to its stabilization.

The effect of counterions on the stability of cationic derivative **4** (M = Cu) was evaluated using complex **7** (M = Cu) containing a BF_4^- anion as an example. As shown by the results of calculations at both levels, the inclusion of a counterion does not affect the stability of the sandwich structure with quasi-planar annulene cycles. At both calculation levels, complex **7** (M = Cu) corresponds to an energy minimum on the PES, and the geometric parameters are changed insignificantly compared to the cationic structure. Structural and energy parameters of complexes **4** (M = Cu) and **7** (M = Cu) are shown in Figure 1 and listed in Table 1.

In the case of a nickel complex, as shown by the results of calculations at both levels of approximation, structure **4** (M = Ni) with D_{5h} symmetry corresponds to a stationary point of the first order (λ = 1), while structure **8** (M = Ni) with reduced symmetry (C_{5h}) corresponds to an energy minimum (see Figure 1, Table 1).



4 (M = Cu), D_{5h} **7** (M = Cu), C_1

4 (M = Ni), D_{5h} **8** (M = Ni), C_{5h}

Figure 1 Geometric characteristics (bond lengths in angstroms) of systems **4**, **7**, and **8** calculated using B3LYP and M06 (values in italic) methods with a 6-311+G(df,p) basis set.

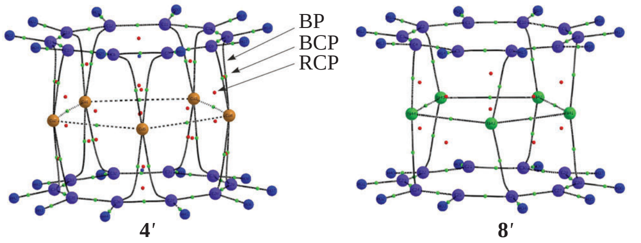
Table 1 Energy parameters[a] of systems **4**, **7**, and **8** calculated using B3LYP and M06 (values in italic) methods with a 6-311+G(df,p) basis set.

Structure	E_{tot}	ZPE	ΔE	λ	ω_1	Δ_{H-L}
4 (M = Cu), D_{5h}	–8976.576707	0.342490	0	0	83.9	2.48
	–8975.512938	*0.340828*	*0*	*0*	*83.7*	*2.87*
7 (M = Cu), C_1	–9401.366926	0.356752	0	0	24.0	2.49
	–9400.168034	*0.356185*	*0*	*0*	*31.9*	*2.87*
4 (M = Ni), D_{5h}	–8315.821533	0.344420	0.47	1	i79.7	2.73
	–8314.783912	*0.343297*	*0.21*	*1*	*i75.2*	*3.39*
8 (M = Ni), C_{5h}	–8315.822288	0.344722	0	0	64.8	2.79
	–8314.784251	*0.343629*	*0*	*0*	*75.5*	*3.42*

[a] E_{tot} (in atomic units) is the total energy, ZPE (in atomic units) is the harmonic zero-point energy correction, ΔE (in kcal mol^{-1}) is the relative energy, λ is the number of negative Hessian eigenvalues, ω_1 (in cm^{-1}) is the value of the lowest harmonic vibration frequencies, and Δ_{H-L} (in eV) is the HOMO–LUMO energy gap.

Unlike system **4** (M = Ni), where all M–C bonds are equivalent, in system **8** (M=Ni) two sets of bonds are formed, the lengths of which differ slightly and are 2.007 (B3LYP)/1.990 (M06) Å for one group of bonds and 2.101 (B3LYP)/2.062 (M06) Å for the other one. These parameters are comparable to the Ni–C bond lengths in known nickel sandwich derivatives (for example, 2.05 Å in benzene complex[36]). As in the case of a copper derivative, the carbon rings of the annulene fragments are practically planar, and the hydrogen substituent atoms are slightly deviated in the direction opposite to the plane of the metal atoms. The alternation of C–C bonds is insignificant: the bonds of one group are 1.413 (B3LYP)/1.408 (M06) Å, and the bonds of the other group are 1.440 (B3LYP)/1.435 (M06) Å. The Ni–Ni distances of the central cycle are 2.560 (B3LYP)/2.523 (M06) Å, exceed the bond length in a Ni_2 dimer (2.15 Å according to experimental data[37]) and are in the range of Ni–Ni bond lengths in various organonickel derivatives (2.29–2.60 Å[34]).

According to the AIM analysis (molecular graphs are shown in Figure 2), each copper atom in complex **4** (M = Cu) forms bond paths with two neighboring copper atoms and four carbon atoms. In the case of the nickel complex, the distortion of the D_{5h}-symmetry structure towards the low-symmetry system ensures a decrease in the coordination number of nickel: each nickel atom in complex **8** (M = Ni) forms four bond paths, that is with neighboring metal atoms and with two carbon atoms. Table 2 lists the calculated AIM parameters for critical bond points (BCPs) corresponding to metal–carbon and metal–metal interactions. One can see from the table that the bond critical points are characterized by positive value of the electronic Laplacian $\nabla^2\rho(r)$, which is usually attributed to closed-shell type interactions.[29] At the same time, the values of the electron density $\rho(r)$ at the BCP points are substantial, and the negative sign of the total electron energy density $H(r)$ indicates the covalent nature of the bonds. These characteristics are associated with so-called 'charge–shift type bonds'[38] which in the AIM theory terms can be considered as an intermediate type between closed-shell and shared interactions. The ratio between the kinetic and



4′ **8′**

Figure 2 Bader molecular graphs **4′** and **8′** of structures **4** (M = Cu) and **8** (M = Ni), respectively; BP designates the Bader bond path, BCP denotes the bond path critical point, and RCP stands for the ring critical point.

Table 2 Wiberg bond indices (WBI) and AIM parameters (atomic units)[a] for the bond critical point (BCP) corresponding to the bonds in systems **4** (M = Cu) and **8** (M = Ni) calculated using B3LYP and M06 (values in italic) methods with a 6-311+G(df,p) basis set.

Structure	Bond	WBI	$\rho(r)$	$\nabla^2\rho(r)$	$H(r)$	$-G(r)/V(r)$
4 (M = Cu)	Cu–C	0.19	0.078	0.222	–0.021	0.784
		0.19	*0.084*	*0.243*	*–0.023*	*0.777*
4 (M = Cu)	Cu–Cu	0.01	0.020	0.047	–0.002	0.875
		0.01	*0.024*	*0.253*	*–0.004*	*0.810*
8 (M = Ni)	Ni–C	0.25	0.094	0.219	–0.029	0.741
		0.25	*0.098*	*0.240*	*–0.031*	*0.752*
8 (M = Ni)	Ni–Ni	0.13	0.039	0.047	–0.014	0.641
		0.12	*0.041*	*0.050*	*–0.015*	*0.651*

[a] $\rho(r)$ is the electron density, $\nabla^2\rho(r)$ is the Laplacian of the electron density, $H(r)$ is the total electron energy density, $V(r)$ is the potential electron energy density, and $G(r)$ is the kinetic electron energy density.

potential energy densities, $-G(r)/V(r)$, which is in the range of 0.5–1 (Table 2), also indicates[39] the partially covalent nature of the bonding. The calculated values of the Wiberg bond index (WBI)[40] confirm the conclusion about a partially covalent bonding nature in the considered complexes (see Table 2).

According to the results of NBO analysis (Table 3), metal atoms interact with hydrocarbon cycles by donating electron density from filled d-orbitals of metal atoms to antibonding orbitals of C–C bonds [Figure 3(*a*)]. In addition, back donation from the bonding orbitals of C–C bonds to the hybrid orbitals (with predominant s-character) of metal atoms occurs in these systems [Figure 3(*b*)]. The results of MO-analysis confirm the stabilizing role of interactions between the orbitals of the π-system of annulene rings and the central fragment (see Figure S1 in Online Supplementary Materials). The values of the energy gap between the frontier orbitals (see Table 1) also indicate a significant kinetic stability of the considered sandwich complexes.

The calculated NICS(0) indices[41] at the centers of cyclic fragments have negative values (Table 4), pointing to the presence of diatropic ring currents in these regions, and confirm aromaticity of the annulenes and metal cycles. In the case of the copper complex, the NICS(0) index at the centers of hydrocarbon cycles is –21 ppm at both levels of approximation. For the nickel complex, the calculated index NICS(0) is significantly lower (–9 ppm at both levels) to indicate a decrease in the aromaticity of the nickel derivative. Aromaticity of cyclic fragments is an additional stabilization factor for the considered sandwich complexes.

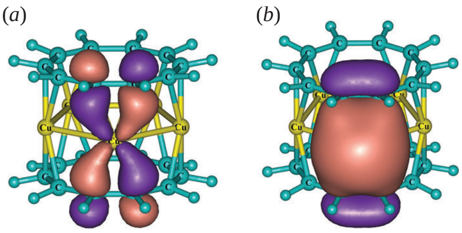


Figure 3 Schematic representations of NBOs responsible for formation of the sandwich structures **4**: (*a*) σ-donation and (*b*) σ-back-donation.

Table 3 Average values of second-order interaction energies [*E*(2), kcal mol^{-1}] between donor and acceptor orbitals[a] in systems **4** (M = Cu) and **8** (M = Ni) calculated using B3LYP and M06 (values in italic) methods with a 6-311+G(df,p) basis set.

Structure	Donor → acceptor	*E*(2)
4 (M = Cu)	LP (Cu) → BD*(CC)	17.0 *18.9*
	BD(CC) → LV(Cu)	50.8 *57.2*
8 (M = Ni)	LP (Ni) → BD*(CC)	31.3 *35.9*
	BD(CC) → LV(Ni)	30.3 *33.5*

[a] BD – bonding orbital, BD* – antibonding orbital, LP – lone pair orbital, LV – lone vacancy orbital.

Table 4 NICS(0) indices (ppm) for annulene (a) and metallic (m) cycles of systems **4** (M = Cu) and **8** (M = Ni) calculated using B3LYP and M06 (values in italic) methods with a 6-311+G(df,p) basis set.

Structure	NICS (a)	NICS (m)
4 (M = Cu)	–20.7 *–20.7*	–30.7 *–31.4*
8 (M = Ni)	–9.1 *–9.2*	–19.4 *–19.5*

To sum up, the performed calculations predict the stability of polyatomic copper $[Cu_5(C_{10}H_{10})_2]^+$ and nickel $Ni_5(C_{10}H_{10})_2$ sandwich complexes, which represent a previously unstudied new type of organometallic compounds with planar [10]annulene rings. The stabilization of the considered complexes is provided by both steric (rigid framework) and electronic (donor–acceptor orbital interactions and aromaticity) effects.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.04.002.

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