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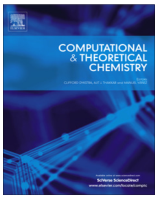

Planar tetracoordinate carbon $\mathrm{CNi_4H_4}$ cluster and its nanoribbon complexes $[(\mathrm{CNi_4H_2})_n(\mathrm{C_4H_6})_{n+1}]$ ($n = 1–4$) stabilized using aromatic butadiene ligands

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ABSTRACT

We report a density-functional study on planar tetracoordinate carbon (ptC) cluster $\mathrm{CNi_4H_4}$ and its nanoribbon complexes $[(\mathrm{CNi_4H_2})_n(\mathrm{C_4H_6})_{n+1}]$ ($n = 1–4$), in which ptC $\mathrm{CNi_4}$ units are separated, interconnected, and stabilized via aromatic butadiene ligands. Simplified as an 18-electron system, ptC $\mathrm{CNi_4H_4}$ cluster features four peripheral Ni–H–Ni three-center two-electron (3c-2e) σ bonds and three-fold (2π, 2σ, and 6σ) aromaticity. The 2π subsystem is situated on inner $\mathrm{CNi_4}$ core, 2σ is located at peripheral $\mathrm{Ni_4H_4}$ ring and oriented tangentially, and 6σ sextet is global in nature and oriented radially. The $[(\mathrm{CNi_4H_2})_n(\mathrm{C_4H_6})_{n+1}]$ ($n = 1–4$) nanoribbons span from 6.60 to 25.69 Å in length, which contain isolated ptC $\mathrm{CNi_4H_2}$ units, being interconnected edge-by-edge via butadiene ligands. Chemical integrity of $\mathrm{CNi_4H_2}$ and butadiene are maintained in the nanoribbons, except for two Ni–C σ bonds per ligand. Nanoribbon complexes represent a new type of extended low-dimensional nanomaterials using the ptC $\mathrm{CNi_4}$ unit.

1. Introduction

Planar tetracoordinate carbon (ptC) molecules [1–6] constitute the core of planar hypercoordinate chemistry [7–13]· which challenge the conventional idea of tetrahedral carbons (thCs), as well as offer potential materials with unusual electronic and magnetic properties. The concept of ptC was first introduced by Monkhorst in 1968 [1]. Hoffmann et al. proposed in 1970 the strategies to stabilize ptC, both electronical and mechanical [2], which represents a milestone work in the field. Nearly 30 years later, Wang and Boldyrev [4–6] successfully produced and characterized a series of simple ptC clusters ($\mathrm{NaCAl_4^-}$, $\mathrm{CAl_3Si^-}$, and $\mathrm{CAl_3Ge^-}$) in gas phase. Relevant isoelectronic *cis*-$\mathrm{CSi_2Al_2}$, *trans*-$\mathrm{CSi_2Al_2}$ species were actually predicted earlier by Schleyer and Boldyrev [14]. These pentaatomic ptC species follow the 18-electron counting. Additional 18-electron ptCs and planar pentacoordinate carbons (ppCs), such as $\mathrm{CE_4^{2-}}$ (E = Al–Tl), $\mathrm{CAl_3E}$ (E = P–Bi), $\mathrm{CAl_5^+}$, $\mathrm{CAl_3Be_2^-}$, and $\mathrm{CBe_5Li_n^{n-4}}$ ($n = 1–5$), were also computed [15–19]. Recently, $\mathrm{CAl_4MX_2}$ (M = Zr, Hf; X = F–I, $\mathrm{C_5H_5}$) clusters with ppC bonded to a transition metal and embedded in a metallocene framework were predicted by Ding and Merino [20]. Fulfillment of the 18-electron rule and electron delocalization is found to be crucial for the species

Clusters with a ptC center surrounded by four transition metal atoms as ligands appear to be rare in the literature [21–27]. In 1991, Musanke and coworkers synthesized a ternary $\mathrm{Ca_4Ni_3C_5}$ carbide crystal [21], which contains a highly unusual ptC $\mathrm{CNi_4}$ moiety, forming one-dimensional, vertex-sharing chains of planar $\mathrm{Ni_4}$ squares. This intriguing ptC structure motivated an extended Hückel tight-binding theory study by Hoffmann and coworkers [22], who analyzed the chemical bonding in the carbide using a square-planar $\mathrm{CNi_4^{4-}}$ model cluster. It was concluded that bonding in $\mathrm{CNi_4^{4-}}$ resembles that in ptC $\mathrm{CH_4}$ species, implying that Ni $\mathrm{d^{10}}$ configuration is largely maintained in $\mathrm{CNi_4^{4-}}$. Nonetheless, the essence of bonding in the system requires further, in-depth analyses as far as we are concerned. Subsequently, Li et al. [23] proposed to stabilize ptC $\mathrm{CNi_4^{4-}}$ in the form of “hydrometal”, that is, D_{4h} $\mathrm{CNi_4H_4}$, in which π delocalization was revealed as a crucial bonding mechanism. One of the present authors also explored the possibility to stabilize ptC $\mathrm{CNi_4^{4-}}$ using bridging Cl ligands in the form of $\mathrm{CNi_4Cl_4}$ [24]. Compared to $\mathrm{CNi_4H_4}$, the $\mathrm{CNi_4Cl_4}$ cluster showed enhanced Ni–C–Ni bonding due to the participation of Cl 2p atomic orbitals (AOs) in π delocalization. Furthermore, square-sheet sandwich complexes [26] and extended low-dimensional

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nanomaterials [27] based on ptC CNi_4 or CNi_4H_4 were also studied computationally, the latter featuring edge-sharing Ni_4 squares.

In this contribution, we report a density-functional theory (DFT) study on a series of nanoribbon complexes $[(CNi_4H_2)_n(C_4H_6)_{n+1}]$ (n = 1–4), in which ptC CNi_4 is stabilized using π aromatic butadiene ligands. In such complexes, each ptC CNi_4 unit is coordinated by two butadiene ligands in an in-plane fashion along two opposite Ni_2 edges, and the remaining two Ni_2 edges are passivated by two H bridges. All ptC CNi_4 units are isolated from each other by butadiene chains, forming quasi-one dimensional nanoribbons in which both ptC CNi_4 and butadiene maintain their chemical identity. We also fully analyzed chemical bonding in ptC CNi_4H_4 cluster and proposed a bonding model for this exotic species, featuring three-fold (π and σ) aromaticity. The bonding model differs from existing knowledge regarding this ptC system.

2. Methods

Cluster structures were constructed manually and full optimizations were performed at the B3LYP/def2-TZVP level [28,29]. Frequency calculations were done at the same level to ensure that the reported structures are true minima. Natural bond orbital (NBO) analyses [30] were carried out at B3LYP/def2-TZVP to obtain natural atomic charges and Wiberg bond indices (WBIs).

The present cluster systems are expected to be well-behaved for DFT. B3LYP as a mature density functional should work. Nonetheless, we chose to test and confirm this using an alternative PBE0/def2-TZVP method [31], which is generally considered to be complementary to B3LYP. Test calculations at PBE0 are presented in Supplementary Material (Fig. S1), which are highly consist with those at B3LYP (Fig. 1), in terms of bond parameters, normal vibrational frequencies, natural atomic charges, and WBIs. We will thus focus on B3LYP data only in this paper.

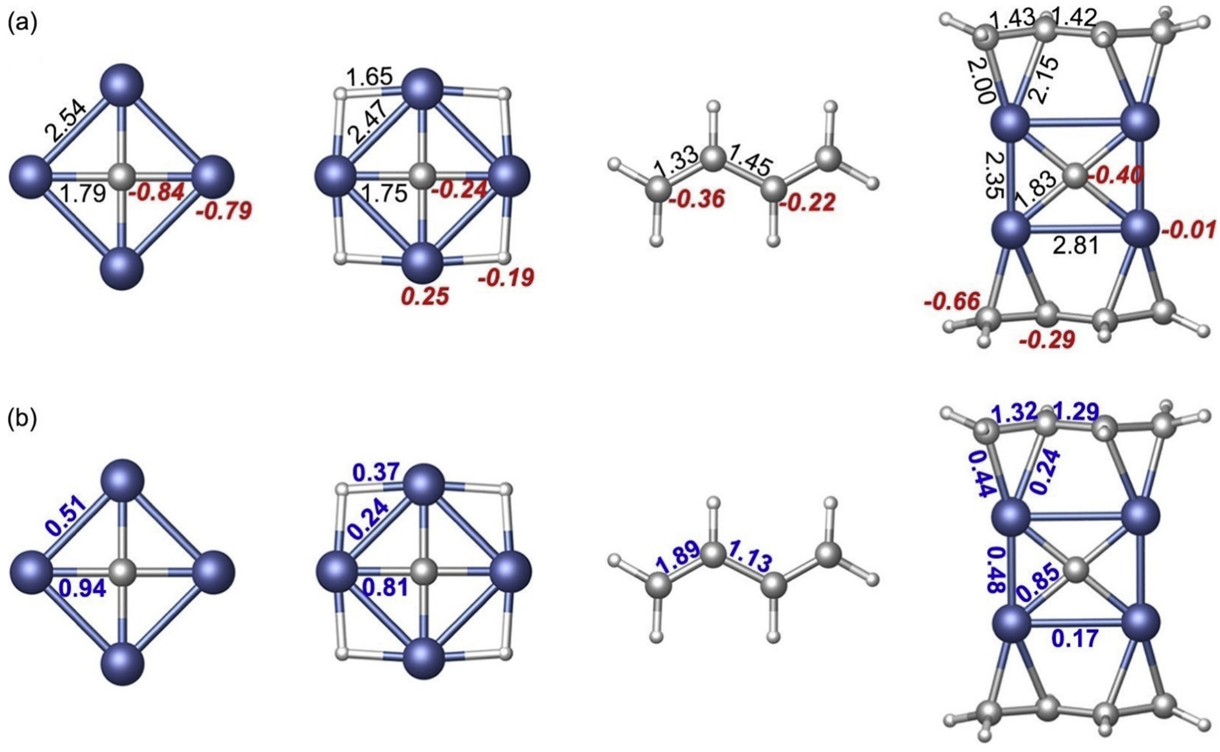
Canonical molecular orbital (CMO) analysis and orbital composition calculations were carried out to gain insight into chemical bonding, the latter using the Multiwfn program [32]. Nucleus independent chemical shifts (NICSs) [33] were calculated to assess π/σ aromaticity for the species. Infrared spectra were simulated for the nanoribbon complexes at B3LYP/def2-TZVP level. All electronic structure calculations were done using Gaussian 09 [34]. Molecular structures and CMOs were visualized using CYLview and GaussView 5.0 [35,36].

3. Results

3.1. CNi_4^{4-}, CNi_4H_4, and C_4H_6: Structural blocks of nanoribbon complexes

The building blocks of nanoribbon complexes $[(CNi_4H_2)_n(C_4H_6)_{n+1}]$ (n = 1–4) are D_{4h} CNi_4^{4-} (**1**), D_{4h} CNi_4H_4 (**2**), and C_{2h} C_4H_6 (**3**). Their optimized structures at B3LYP level are shown in Fig. 1a. The C–Ni and Ni–Ni distances in **2** are 1.75 and 2.47 Å, respectively. According to recommended atomic radii by Pyykkö [37], the upper bounds of C–Ni and Ni–Ni single bonds are 1.85 and 2.20 Å, respectively. Thus C–Ni bond in **2** is close to single bond, whereas Ni–Ni bonding appears to be weak, in line with the findings in literature [21,22]. The peripheral Ni–H distance is 1.65 Å, which is much larger than Ni–H single bond (1.42 Å) [37], consistent with the nature of a bridging H ligand.

The geometry of CNi_4^{4-} (**1**) tetraanion is closely similar to that of **2**, except for a slight expansion of C–Ni and Ni–Ni distances (by 0.04 and 0.07 Å, respectively). This effect is due to substantial



1 D_{4h} CNi_4^{4-} **2** D_{4h} CNi_4H_4 **3** C_{2h} C_4H_6 **4** C_{2h} $[(CNi_4)(C_4H_6)_2]^{2-}$

Fig. 1. Optimized structures at B3LYP/def2-TZVP level of planar tetracoordinate carbon (ptC) CNi_4^{4-} **1** (D_{4h}, $^1A_{1g}$) tetraanion cluster, ptC CNi_4H_4 **2** (D_{4h}, $^1A_{1g}$) cluster, butadiene C_4H_6 **3** (C_{2h}, ^1A_g), and nanoribbon $[CNi_4(C_4H_6)_2]^{2-}$ **4** (C_{2h}, ^1A_g) dianion cluster. Selected bond distances (in Å) and natural atomic charges (in |e|; red color) are shown in the top panels. Shown in the bottom panels are Wiberg bond indices (WBIs; blue color). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)