

M₅H₅X (M = Ag, Au, Pd, Pt; X = Si, Ge, P, S): Hydrometal Pentagons with D_{5h} Planar Pentacoordinate Nonmetal Centers

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Received: June 6, 2005; In Final Form: July 3, 2005

A density functional theory investigation has been presented in this work on M₅H₅X hydrometal pentagons (M = Ag, Au, Pd, P) with D_{5h} planar pentacoordinate nonmetal centers (X = Si, Ge, P, S). The introduction of the nonmetal centers X introduces p aromaticity to M₅H₅X complexes. These novel planar complexes are favored in thermodynamics and confirmed to be aromatic in nature. They may be expanded to one, two, or even three dimensions with multiple planar pentacoordinate silicon and other nonmetal centers.

1. Introduction

The structures and properties of planar tetra-,^{1–7} penta-,^{8,9} and hexacoordinate^{10–12} carbons have aroused great interest among chemists in the past thirty years, while much less attention has been paid to their silicon analogues beyond the traditional tetrahedron concept. Planar tetracoordinate (PT) silicon was first studied about twenty years ago¹³ and recently observed in C_{2v} MAI₄ and MAI₄[–] (M = Si, Ge).¹⁴ Utilizing the frameworks of the polygonal hydrocoppers (Cu_nH_n) proposed by Tsipis et al.,¹⁵ our group recently presented the possibility of hosting PT carbon in squared M₄H₄C (M = Cu, Ni),⁵ planar pentacoordinate (PP) carbon in pentagonal Cu₅H₅X (X = B, C, N, O),⁹ and planar hexacoordinate (PH) silicon in hexagonal Cu₆H₆Si¹⁶ at the density functional theory (DFT) level. Inspired by the novel design of planar pentacoordinate carbons,⁸ we have also proposed a universal structural pattern at DFT to incorporate planar hypercoordinate silicons in the C_{2v} B_nE₂Si series (n = 2–5; E = Si, CH, BH) with Si as periphery atoms in these molecular fans.¹⁷ In this report, we continue the research by exploring the possibility at DFT of hosting D_{5h} PP silicon and other nonmetals at the centers of pentagonal hydrometals M₅H₅^{15,18} to form M₅H₅X complexes with M = Ag, Au, Pd, Pt and X = Si, Ge, P, S. As heavy transition metal elements in group 11 and group 10 in the periodic table, Ag and Au and Pd and Pt are isolobal in valence electron configurations with Cu and Ni, respectively, but they are systematically bigger in atomic size. Pt₅H₅[–] and Pd₅H₅[–] pentagons are found to provide the right cavities to match D_{5h} PP Si and Ge centers both geometrically and electronically. To the best of our knowledge, there has been no investigation reported to date on PP Si or Ge at the center of a perfect pentagon with the high symmetry of D_{5h}. The present work and our previous investigations combined provide strong DFT evidence that polygonal hydro-transition-metals M_nH_n (M = group 10 and 11 transition metals; n = 4–6) may serve as effective ligands to host planar coordinate carbon,

silicon, and other nonmetal atoms at their geometry centers with the high symmetry of D_{nh}.

2. Computational Procedure

Initial structures were optimized using the Gaussian 03 program¹⁹ at the hybrid DFT functional level of B3LYP with the bases of LanL2dz for transition metals (which contains a Los Alamos effective core potential) and 6-311+G(d) for nonmetal atoms. Imaginary vibrational frequencies were checked at the same theoretical level. To assess the aromaticity of the systems, the nucleus independent chemical shifts (NICS)^{20,21} were calculated by using the gauge-independent atomic orbital (GIAO) procedure at B3LYP with the same basis. The vertical one-electron detachment energies of anions were calculated employing the outer valence Green's function (OVGF)²² to facilitate future photoelectron spectroscopic measurements. Figure 1 depicts the optimized structures (upper) of the Ag₅H₅X series (X = Si, P, S) and their highest occupied molecular orbital (HOMO) pictures (lower) and Figure 2 shows the optimum geometries of Au₅H₅P⁺, Pt₅H₅Ge[–], and M₅H₅Si[–] (M = Pd, Pt) and their lithium salts LiM₅H₅Si. Four typical delocalized out-of-plane molecular orbitals (MOs) of D_{5h} Pt₅H₅Si[–] are shown in Figure 3. The important DFT bond lengths, lowest vibrational frequencies, Wiberg bond indices of the X centers, NICS(1) values calculated with ghost atoms located 1.0 Å above the M₅ planes (the structural centers have been occupied by X atoms), and the low-lying one-electron vertical detachment energies of anions are summarized in Table 1. The reversed values of the HOMO energies listed in Table 1 approximately represent the ionization potentials (IPs) of corresponding complexes in Koopmans' theorem. Their HOMO-LUMO energy gaps are also tabulated in Table 1.

3. Results and Discussions

As shown in Figure 1, Figure 2, and Table 1, D_{5h} Ag₅H₅P⁺, Au₅H₅P⁺, Ag₅H₅S²⁺, and Au₅H₅S²⁺ are all true minima on their

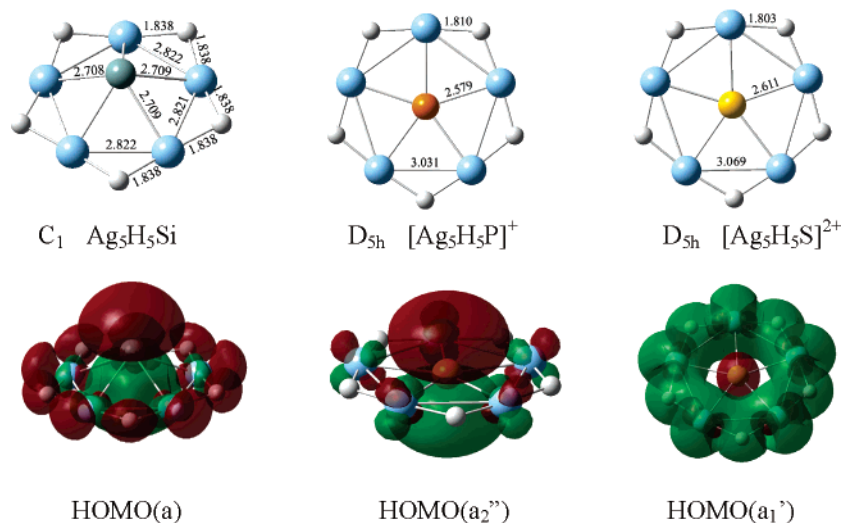


Figure 1. Optimized structures (upper) and corresponding HOMO pictures (lower) of $\text{Ag}_5\text{H}_5\text{X}$ neutral and cations ($\text{X} = \text{Si}, \text{P}, \text{S}$).

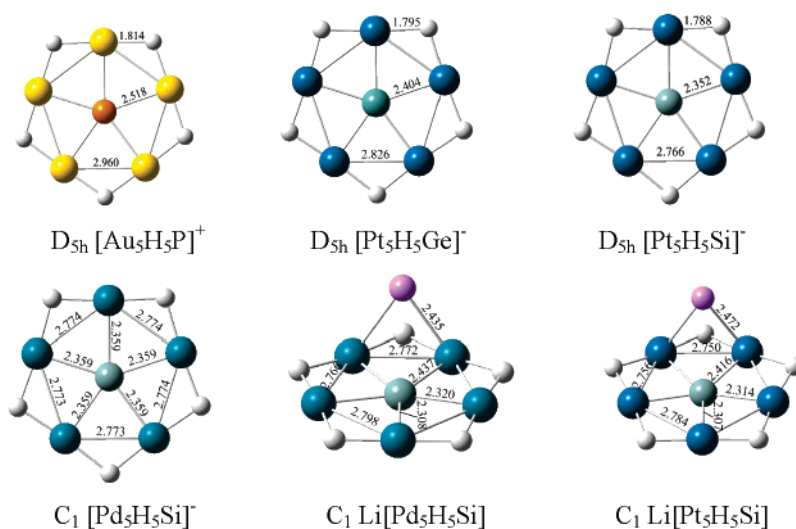


Figure 2. Optimum geometries of $[\text{Au}_5\text{H}_5\text{P}]^+$, $[\text{Pt}_5\text{H}_5\text{Ge}]^-$, and $[\text{M}_5\text{H}_5\text{Si}]^-$ anions ($\text{M} = \text{Pd}, \text{Pt}$) and their lithium complexes $\text{Li}[\text{M}_5\text{H}_5\text{Si}]^-$.

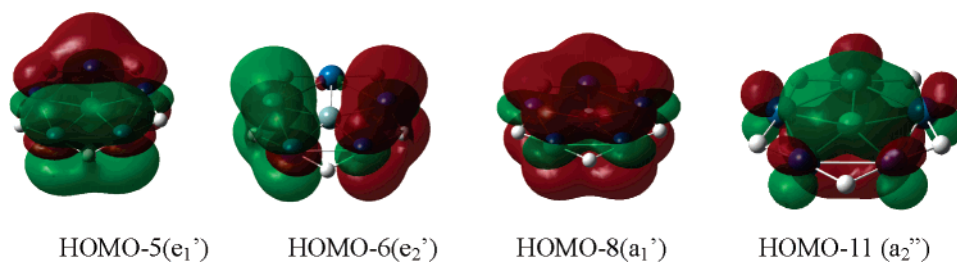


Figure 3. Four typical delocalized out-of-plane MOs of $\text{D}_{5h} \text{Pt}_5\text{H}_5\text{Si}^-$.

potential energy surfaces without imaginary vibrational frequencies. But a $\text{D}_{5h} \text{Ag}_5\text{H}_5\text{Si}$ turned out to be a transition state with one imaginary frequency at $95i \text{ cm}^{-1}$ (an a_2'' vibrational mode with the Si center vibrating up and down along the 5-fold molecular axis perpendicular to the Ag_5 plane) and a $\text{D}_{5h} \text{Au}_5\text{H}_5\text{Si}$ is a third-order stationary point with three imaginary frequencies at $341i$, $320i$, and $116i \text{ cm}^{-1}$. However, the optimizations of both $\text{C}_{5v} \text{Ag}_5\text{H}_5\text{Si}$ and $\text{C}_{5v} \text{Au}_5\text{H}_5\text{Si}$ had convergence problems at the DFT level used in this work. Totally removing the symmetry constraints during structural optimization, we obtained two C_1 pentagonal pyramid structures for $\text{Ag}_5\text{H}_5\text{Si}$ and $\text{Au}_5\text{H}_5\text{Si}$, which possess the approximate symmetry of C_{5v} (see Figure 1) with Si atoms located about 1.2 \AA above the transition metal planes. Orbital analyses indicate

that a $\text{D}_{5h} \text{Ag}_5\text{H}_5\text{P}^+$ possesses 2 π electrons in its HOMO (a_2'') and therefore conforms with the $(4n + 2)\pi$ electron counting rule, while the approximate $\text{C}_{5v} \text{Ag}_5\text{H}_5\text{Si}$ has a distorted π HOMO in its ground-state structure (see Figure 1). Although the HOMO of $\text{D}_{5h} \text{Ag}_5\text{H}_5\text{S}^{2+}$ is an in-plane delocalized bond (a_1'') composed mainly of the Ag 4d atomic orbitals (AOs) and H 1s AOs, its HOMO-1 (a_2'') turns out to be a delocalized π MO. The π MOs of these complexes are mainly composed of the contributions from the $3p_z$ AOs of the nonmetal centers Si, P, and S, respectively. A similar situation happens to $\text{Au}_5\text{H}_5\text{Si}$, $\text{Au}_5\text{H}_5\text{P}^+$, and $\text{Au}_5\text{H}_5\text{S}^{2+}$. Obviously, both hydrosilver Ag_5H_5 and hydrogold Au_5H_5 are unsuitable to host the much concerned D_{5h} PP Si at their geometrical centers. This situation is similar to that of the $\text{Cu}_4\text{H}_4\text{X}$ series ($\text{X} = \text{B}, \text{C}, \text{N}, \text{O}$),⁵ in which

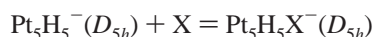
TABLE 1: Optimized Important Bond Lengths, r_{X-M} and r_{M-M} , the Lowest Vibrational Frequencies, V_{\min} , Total Wiberg Bond Indices of the X Centers (WBI_X), Calculated NICS(1) Values, HOMO Energies, and HOMO-LUMO Energy Gaps (Gap) of the Complexes Studied in This Work and the Low-Lying One-electron Vertical Detachment Energies (VDEs) of $M_5H_5X^-$ Anions with Pole Strengths Greater than 0.90 at DFT

	symmetry	r_{X-M} (Å)	r_{M-M} (Å)	V_{\min} (cm ⁻¹)	WBI _X	NICS(1) (ppm)	HOMO (eV)	gap (eV)	VDEs (eV)
Ag ₅ H ₅	~ D_{5h}		2.87	30		-0.6	-7.56	5.76	
Ag ₅ H ₅ Si	~ C_{5v}	2.71	2.82	40	2.1	-11.0	-4.63	1.33	
Ag ₅ H ₅ P ⁺	D_{5h}	2.58	3.03	45	2.2	-6.9	-9.99	2.09	
Ag ₅ H ₅ S ²⁺	D_{5h}	2.61	3.07	48	1.77	-15.6	-15.7	2.43	
Au ₅ H ₅	~ D_{5h}		2.77	38		-1.4	-8.05	5.48	
Au ₅ H ₅ Si	~ C_{5v}	2.68	2.75	11	2.3	-6.8	-4.68	1.41	
Au ₅ H ₅ P ⁺	D_{5h}	2.52	2.96	38	2.31	-11.1	-9.89	2.27	
Au ₅ H ₅ S ²⁺	D_{5h}	2.54	2.98	46	2.0	-15.5	-16.2	3.12	
Pd ₅ H ₅ Si ⁻	~ D_{5h}	2.36	2.77	10	3.46	-0.3	-2.14	2.46	4.88(e ₂ '), 5.49(e ₁ ')
Pd ₅ H ₅ Ge ⁻	~ D_{5h}	2.42	2.84	21	3.34	-2.3	-2.13	2.33	4.80(e ₂ '), 5.47(e ₁ ')
Pt ₅ H ₅ ⁻	D_{5h}		2.62	17		+107	-2.32	1.16	
Pt ₅ H ₅ Si ⁻	D_{5h}	2.35	2.77	38	3.69	-6.2	-2.36	2.34	5.16(e ₂ '), 5.61(a ₂ '), 5.93(e ₁ ')
Pt ₅ H ₅ Ge ⁻	D_{5h}	2.40	2.83	40	3.58	-8.2	-2.45	2.26	5.10(e ₂ '), 5.95(e ₁ ')
Pt ₅ H ₅ P	C_s	2.33	2.74	9	3.75	-11.6	-6.80	2.03	
Li[Pd ₅ H ₅ Si]	~ C_s	2.32	2.77	11	3.48	+1.4	-5.96	2.58	
		2.44	2.80						
Li[Pt ₅ H ₅ Si]	~ C_s	2.31	2.75	36	3.75	-8.8	-6.13	2.45	
		2.42	2.78						

Cu₄H₄B⁻ and Cu₄H₄C prefer C_{4v} pyramids to D_{4h} squares, while Cu₄H₄N⁺ and Cu₄H₄O²⁺ take planar squared structures with the high symmetry of D_{4h} .

Extensive searches at DFT indicate that the long-sought D_{5h} planar pentacoordinate silicon can be stabilized at the centers of both D_{5h} Pt₅H₅Si⁻ and C_1 Pd₅H₅Si⁻ (which has the actual symmetry of D_{5h} at DFT) as shown in Figure 2, with the bond lengths of $r_{Si-M} \approx 2.35$ and $r_{M-M} \approx 2.77$ Å. These pentagonal complexes contain D_{5h} Si centers with five transition-metal ligands evenly distributed around them. Similarly, D_{5h} Ge centers can be stabilized in perfect pentagons Pt₅H₅Ge⁻ and Pd₅H₅Ge⁻ with the Ge-M bond lengths close to 2.40 Å. Introducing an alkaline counterion Li⁺ into M₅H₅Si⁻ (M = Pd and Pt), we obtained two C_1 structures with the approximate symmetry of C_s for Li[Pd₅H₅Si] and Li[Pt₅H₅Si] (see Figure 2), in which the planar M₅H₅Si⁻ structural units and PP Si centers are well maintained. The calculated natural charges of Li atoms in these complexes are found to be close to +0.90|e| and these alkaline cations form ionic bonds with the planar M₅H₅X⁻ structural cores. As indicated by the total Wiberg bond indices ranging from WBI_X = 3.34 to 3.75 (see Table 1), the D_{5h} Si, Ge, and P centers in these planar M₅H₅X complexes (M = Pd, Pt) follow the octet rule in interacting with the transition metal ligands.

Concerning the stability of D_{5h} Pt₅H₅X⁻ (X = Si, Ge) complexes, the following reaction



has the calculated DFT energy changes of $\Delta E = -810.8$, -935.9 , enthalpy changes of $\Delta H = -814.0$, -940.6 , and free Gibbs energy changes of $\Delta G = -767.6$, -894.1 kJ/mol for X = Ge and Si, respectively. Obviously, pentagonal Pt₅H₅X⁻ complexes with D_{5h} Si and Ge centers are strongly favored in thermodynamics with respect to a Pt₅H₅⁻ anion and a free X atom.

The negative NICS(1) values tabulated in Table 1 indicate that the M₅H₅X complexes studied in this work are aromatic in nature, except for Li[Pd₅H₅Si], which has a slightly positive NICS value (+1.4 ppm), partially explaining the stability of these nonmetal-atom-centered planar molecules. These NICS(1) values are comparable with the corresponding values of benzene (-10.1 ppm at the same theoretical level). It is interesting to notice that M₅H₅X complexes have higher negative

NICS values than the corresponding hydrometals M₅H₅ in all cases for the reason that the introduction of X centers introduces p aromaticity to the M_nH_nX complexes. For instance, as clearly indicated in Figure 1, Ag₅H₅X complexes (X = Si, P, S) possess 2 π electrons in their HOMO or HOMO-1 which are mainly composed of the contribution of the 3p_z orbitals of the nonmetal centers. In the case of Pt₅H₅Si⁻, the π -type HOMO-11(a₂'') (see Figure 3) mainly reflects the contribution of Si 3p_z AO. It should be pointed out that the d aromaticity existing in M₄H₄ and Li₂M₄²⁺ should exist in the M₅H₅X complexes (X = Ag, Au, Pd, Pt) studied in this work. In the four typical delocalized out-of-plane MOs of Pt₅H₅Si⁻ shown in Figure 3, HOMO-5 and HOMO-6 consist purely of Pt 5d_{z²} contributions, while HOMO-8, which is dominated by the in-phase overlap of Pt 5d_{z²} AOs, also includes the contribution of the Si 3s AO. Two other degenerate antibonding MOs (HOMO-1(e₂'), which are not shown in Figure 3) represent the out-of-phase interactions of the five Pt 5d_{z²} AOs.

4. Summary

In conclusion, we have presented DFT evidence in this work that planar pentacoordinate silicon and other nonmetal centers can be stabilized in perfect pentagonal hydro-transition-metals to form M₅H₅X complexes (M = Ag, Au, Pd, Pt; X = Si, Ge, P, S). These planar complex units are favored in thermodynamics and confirmed to be aromatic in nature. Our M_nH_nX complex series^{5,9,16} containing D_{nh} C, Si and other D_{nh} nonmetal centers coordinated to n transition metal ligands ($n = 4, 5, 6$; M = Cu, Ag, Au, Ni, Pd, Pt) may be expanded to one, two, or even three dimensions with multiple nonmetal centers.

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