MH₅^{0/+/-}: σ Aromatic Cluster

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ABSTRACT Aromaticity is one of the central concepts in chemistry. Herein, quantum chemical calculations have been carried out to search for σ aromatic metal pentahydrides of the general formula MH₅⁻ (M = Ni, Pd, Pt). All these group 10 metals form true local minimum in their planar D_{5h} symmetry. The presence of σ

aromaticity in these clusters were ascertained from molecular orbital, electron density of delocalized bonds (EDDB) and iso-chemical shielding surface (ICSS_{zz}) analyses. Detailed potential energy surface analyses reveal that $D_{\rm 5h}$ geometry of PtH₅⁻ is the lowest energy one while NiH₅⁻ and PdH₅⁻ clusters form stable $C_{\rm 2V}$ dihydrogen M(η^2 -H₂)H₃ complexes. Similarly, M(η^2 -H₂)H₃ geometry of CsH₅ and BaH₅⁺ is the lowest one with aromatic character.



Article

Keywords: σ -aromaticity, metal hydrides, theoretical chemistry, electron density of delocalized bonds, core orbital

INTRODUCTION

Aromaticity needs no introduction to chemists as it is one of the stabilizing bonding effects that is responsible for providing remarkable symmetries and stabilities of clusters and molecules.¹⁻¹⁸ Multiple types of aromaticity, including σ -, π - and δ - type or combination thereof have been reported. The simplest of these is the σ - aromaticity which faced serious objection initially and then accepted and widely explored. One of the simplest examples of σ -aromaticity is the clusters of hydrogen, where bonding overlap between the 1s atomic orbitals (AOs) of H gives rise to this phenomenon. One typical example of such species is the H₃⁺ cluster, a highly abundant interstellar species. Similarly, H_5^- was also predicted to be σ - aromatic,¹⁹ however, the planar D_{5h} structure of H_5^- was found to be saddle point on the potential energy surface. In 2003, Tsipsis and co-workers predicted the existence of aromatic metal hydride clusters MnHn (M = Cu, Ag, Au; n = 3-6).²⁰⁻²³ However, their experimental evidence is still absent. In 2014, Zhang et al.²⁴ showed the existence of σ - aromaticity in ZnPtH₅⁻ cluster using a joint experimental photoelectron spectroscopy and theoretical study. The cluster featured a Pt atom sitting in a plane surrounded by five Hs. The σ -delocalization was stabilized by the overlap of 5d6s6p overlap of Pt atom with the 1s AOs of H. It is interesting to note that Zn atom in ZnPtH5⁻ is a just a spectator metal as the

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orbitals of Zn atom was not involved in the delocalization, rather involved in bonding with Pt center. This sparkled an interest: can we have a true minimum for planar D_{5h} MH₅ cluster? Does all the group 10 (Ni, Pd, Pt) form σ - aromatic cluster? To answer these questions, a thorough theoretical calculation is performed for anionic MH_5^- (M = Ni, Pd, Pt) clusters. Metal hydrides can be found as intermediates in many catalytic processes.²⁵⁻²⁷ Thus, finding even a true local minimum with σ -aromaticity seems attractive. It should be noted that as pointed out by Zhai and Alexandrova,²⁸ cluster catalysis is dominated by fluxionality and therefore, the most stable global minimum geometry may not be as reactive as other local minima. From this perspective, a true local minimum geometry of metal hydrides with σ -aromaticity is very lucrative and worthy of exploring. We have also investigated the possibility of alkali and alkaline earth metal hydrides to investigate the possibility of σ -aromaticity.

Computational Details

As identifying true local minima of the planar D_{5h} structure is the main motivation of this work, different density functionals such as TPSSh,²⁹ B3LYP-D3(BJ),^{30,31} PBE0³² and ω B97XD³³ in combination with def2-TZVP basis set were used for the optimization and frequency calculations. Harmonic vibrational frequency calculations were performed at the same level to understand the nature of stationary points. Local minimum structures were identified with all real values of the Hessian matrix. Electronic structures were analyzed using natural bond orbital (NBO)³⁴ at TPSSh level. All these calculations were performed using Gaussian 16 suite of program.³⁵

Aromaticity of these clusters were evaluated by performing electron density of delocalized bonds (EDDB) calculations using EDDBRun scripts³⁶ and visualized using Avogadro.³⁷ Z-component of iso-chemical shielding surface (ICSS_{zz})³⁸⁻⁴⁰ were analyzed using Multiwfn program code.⁴¹

RESULTS AND DISCUSSION

Let us first investigate the artefact of the level of density functional theory. Table 1 summarizes the results of different density functionals. It is evident from Table 1 that all these density functionals produce true local minimum for D_{5h} structure of NiH₅⁻, PdH₅⁻ and PtH₅ clusters.

Table 1. Results of different density functionals on the D_{5h} geometry of the clusters. Lowest vibrational frequencies (v₁) are in cm⁻¹.

Functional↓/Cluster→	NiH5 ⁻	PdH5	PtH5 ⁻
	ν_1	ν_1	V1
TPSSh	300	361	507
B3LYP-D3(BJ)	167	346	516
PBE0	175	322	501
ωB97XD	63	268	488

It is evident from Table 1 that PtH_5^- alone (that is without Zn) can form a true local minimum in D_{5h} planar structure with significantly high lowest vibrational frequency of 507 cm⁻¹ at TPSSh level and with a sizable HOMO-LUMO gap of 4.7 eV. This inspired to investigate whether other members of the Pt family (Ni and Pd) will form true local minima in their D_{5h} planar structure or not. Figure 1 shows the optimized geometries of MH_{5} (M = Ni, Pd, Pt). All are true local minima with significant lowest vibrational frequencies. All the M-H bond lengths are equal in a particular cluster. Similarly, all the H.H distances are equal. Thus, equality in M-H and H.H distances may be considered to be the geometric criterion for aromaticity. Cationic MH_{5^+} (M = Zn, Cd, Hg) were also tested. However, they all are high order saddle points on the potential energy surface. Similarly, neutral MH₅ (M = Cu, Ag, Au) clusters were also tested. They are also saddle points on the potential energy surface except AuH₅ which is a true local minimum. This implies that group 10 transition metals (Ni, Pd, Pt) and Au are the best candidates to form planar D_{5h} structures.



Figure 1. TPSSh/def2-TZVP optimized local minimum geometry of D_{5h} symmetric MH₅⁻ (M = Ni, Pd, Pt) and AuH₅ clusters. Bond lengths are in Å and lowest vibrational frequencies (v_{lowest}) are in cm⁻¹.

The electronic structure of MH_5^- (M = Ni, Pd, Pt) clusters were then investigated in detail to understand the presence (or absence) of any aromaticity in these clusters. Figure 2 shows the qualitative molecular orbital diagram of MH₅⁻ cluster. HOMO, HOMO-1 and HOMO-3 are clearly metal d lone pairs. Doubly degenerate HOMO-2 and the HOMO-4 constitute the sixelectron counting for σ -aromaticity. All these MH₅⁻ clusters feature similar molecular orbitals and hence are σ -aromatic. The molecular orbitals of PtH₅⁻ are shown in Figure 2b as a representative case. HOMO and the two sets of doubly degenerate HOMO-1 and HOMO-3 are the lone pairs at Pt center while the doubly degenerate HOMO-2 and HOMO-4 are formed by the interaction of 6s6p5d orbitals of Pt with 5 × H 1s ligand group orbitals of H atoms.



Figure 2. Qualitative molecular orbital diagram of (a) $MH_5^{0/+/-}$ clusters and (b) occupied frontier molecular orbitals of PtH_5^- cluster. Contour value used was 0.03 a.u.

In addition to molecular orbital analysis and electron counting, aromaticity in these clusters were also investigated using electron density of delocalized bonds (EDDB).42 EDDB method is based on population analysis of natural orbitals for the delocalized bonds (NOBD) which is similar to population analysis of ncentred-2-electron bonds as implemented in adaptive natural density partitioning (AdNDP) scheme.43 EDDB has been successfully applied to organometallics^{44,45} and various systems.⁴⁶ Iso-chemical shielding surface (ICSS)³⁸⁻⁴⁰ analysis were also performed to investigate aromaticity in these clusters. Figure 3a-b shows the EDDB iso-surface of NiH5, AuH5 and ICSS_{zz} iso-surface of PtH₅⁻ (Figure 3c). EDDB results (Table 2) indicate total population of greater than 2.4 electrons which arises solely due to σ delocalization. Similarly, ICSS_{zz} iso-surface clearly reveals the presence of shielding zone (red region, Figure 3(c)) above and below the molecule plane suggesting that the Zdirection of the external magnetic field is largely shielded in this region, an observation consistent with strong aromaticity.



Figure 3. EDDB(r) iso-surface of (a) NiH₅⁻, (b) AuH₅ (contour value = 0.015 a.u.) and (c) ICSS_{zz} iso-surface of PtH₅⁻ with iso-surface value of 2.2 a. u. Red region: shielding; cyan region: deshielding.

Table 2. Electron densities of delocalized bonds (EDDB) of MH_5^- (M = Ni, Pd, Pt) and AuH_5 clusters. Populations are in electrons.

Cluster	Total populations
	(e)
NiH5 ⁻	2.5
PdH5 ⁻	2.5
PtH5 ⁻	2.4
AuH5	2.4

In 1999, Bayse and Hall predicted the geometries of MH₅⁻ (M = Ni, Pd, Pt) complexes and concluded that $M(\eta^2-H_2)H_3$ complexes are lower in energy than the D_{5h} geometries.⁴⁷ I therefore, calculated the energies of D_{5h} and $C_{2V} M(\eta^2-H_2)H_3$ structures. Figure 4 shows the relative energies of the structures in different symmetries. It is evident from Figure 4 that η^2-H_2 bound C_{2V} structures of NiH₅⁻ and PdH₅⁻ are lower in energy as pointed out by Bayse and Hall,⁴⁷ while the D_{5h} structure of PtH₅⁻ is lower in energy than the C_{2V} geometries. Thus, NiH₅⁻ and PdH₅⁻ prefer η^2 -H₂ complexes while PtH₅⁻ prefers perfect D_{5h} structure. However, owing to the small energy differences, it is expected that both these C_{2V} and D_{5h} structures will be almost equally populated in the experimental condition.



Figure 4. Relative energies (kcal/mol, shown within parenthesis) of the C_{2V} and D_{5h} structures of MH₅⁻ (M = Ni, Pd, Pt) clusters.

Neutral σ aromatic MH₅ cluster may be achievable with Au. Thus, the presence of d-orbital may provide stability to the D_{5h} geometry of MH5 clusters which results in the identification of true local minima of planar D_{5h} geometry. However, η^2 -H₂ complex of AuH₅ is also lower in energy by 12.3 kcal/mol compared to the D_{5h} structure. This indicates that D_{5h} structure of AuH₅ will have lower population in the experimental condition. Is a transition metal necessary to achieve σ aromaticity in MH₅ cluster? Can alkali or alkali earth metals serve the purpose? Very recently, Frenking and co-workers revealed the particular role of (n-1)d AOs of heavier group 2 metals in chemical bonding.⁴⁸⁻⁵² Therefore, cationic MH_{5^+} (M = Ca, Sr, Ba) clusters were investigated. Out of these three combinations, only BaH5⁺ was found to possess a true local minimum in its D_{5h} symmetry at these DFT levels (Table S1, supporting information). Similarly, the iso-electronic CsH5 was also found to be true local minimum in D_{5h} symmetry. Others are high order saddle points. Figure 5 shows the optimized local minimum geometry of BaH5⁺ and CsH₅ along with occupied molecular orbitals. Unlike transition metal hydrides discussed above, no C2v structure is located in the potential energy surface of CsH5 and BaH5+ clusters. All the Cs-

H and H.H distances are same in CsH₅ cluster and similar geometrical feature is also observed for BaH5+ cluster. The lowest vibrational frequency of CsH₅ cluster is 525 cm⁻¹ while that for BaH5⁺ cluster is 540 cm⁻¹ at TPSSh level (Table S1). Molecular orbital analysis reveals that the doubly degenerate HOMO originated from (n-1)d orbital and the HOMO-2 originated from np AOs are lone pairs at the Cs (Ba) center. HOMO-1 is formed by overlap of ns and (n-1)d orbital of Cs (Ba) center with H ligand group orbitals while the doubly degenerate HOMO-3 has contribution from np AO of Cs (Ba) center. HOMO-1 and the doubly degenerate HOMO-3 constitute the 6σ aromatic character of CsH5 and BaH5⁺ clusters. The role of (n-1)d orbital of heavier alkali and alkali earth metal48-52 in aromatic delocalization is clearly evident. The aromaticity of these clusters has also been assigned from EDDB and ICSSzz analysis (Figure 6). The total population of EDDB for CsH5 and BaH5⁺ are 2.9 and 2.8 electrons (Figure 6a-b). Similarly, significant positive value (> 20 ppm) in the 2D-plot (Figure 6c) of ICSSzz and the presence of shielding zone above and below the molecular plane in the 3D plot (Figure 6d), a clear signature of σ aromaticity. Thus, higher total population of EDDB for CsH5 and BaH5⁺ clusters compared to other transition metal clusters indicate that the former two are more aromatic than the later.



Figure 5. (a) Optimized local minimum geometries of CsH₅ and BaH₅⁺ clusters. Bond lengths are in Å, (b) qualitative molecular orbital diagram of CsH₅ and BaH₅⁺ clusters and (c) occupied frontier molecular orbitals of CsH₅ cluster (as a representative case). Contour value used was 0.03 a.u.



Figure 6. EDDB(r) iso-surface of (a) CsH₅, (b) BaH₅⁺ (contour value = 0.015 a.u.), (c) 2D-plot of ICSS_{zz} iso-surface of CsH₅ and (d) 3D-plot of ICSS_{zz} iso-surface for BaH₅⁺ with contour value of 2.2 a. u. Red region: shielding; yellow region: deshielding.

The electronic structures of CsH₅ and BaH₅⁺ clusters are interesting as it involves the core electrons of Cs and Ba. Involvement of only valence electrons in chemical bonding is by far the most acceptable notion in chemical bonding. However, elements down the group may show some anomaly due to small energetic separation between the potentially occupied levels. Natural population analyses (NPA) reveal that Cs and Ba atoms $5p_x^{1.58}5p_y^{1.58}5p_z^{1.99}6s^{0.21}$ $5p_x^{1.72}5p_y^{1.72}5p_z^{1.99}6s^{0.23}$ have and configurations respectively. This implies that the core 5px and 5py along with the 6s orbital of Cs and Ba are involved in the bonding with the $5 \times H1s$ ligand group orbitals. Since the molecule lies in the XY plane, core 5pz orbital remains as lone pair. This is a unique feature of these clusters as involvement of core electrons were predicted at high pressure. But these are examples at p = 1atm. Similar involvement of core electrons in chemical bonding at p = 1 atm were also predicted for CsF₂⁺ and CsF₅ by Hoffmann and co-workers.53

CONCLUSION

In summary, density functional theory has been applied to search for real minima of planar MH5⁰/+)- clusters. The present calculations reveal that all the group 10 transition metals (Ni, Pd, Pt) result in planar D_{5h} structures as true local minima for anionic MH₅⁻ cluster. However, the D_{5h} structure of PtH₅⁻ is the global one while $M(\eta^2-H_2)H_3$ for M = Ni and Pd are the lowest energy one. Although neutral AuH5 also features a true local minimum in D_{5h} planar structure, however the Au(η^2 -H₂)H₃ is lower in energy by 12.3 kcal/mol. Although local minimum, but all these planar clusters are σ aromatic which has been confirmed by EDDB and ICSS_{zz} as well as molecular orbital analyses. The present study also highlights the fact that alkali metals like Cs and Ba can also form true local minima in D_{5h} geometry with significant aromaticity. The particular role of (n-1)d orbital of Cs and Ba results in stabilizing the planar form. Alkali and alkaline metal supported H₅ clusters are more aromatic as evident from EDDB analyses. CsH5 and BaH5+ clusters possess unique chemical feature as Cs and Ba involve their core electrons in chemical bonding, a rare phenomenon at ambient pressure. The present study accumulates several examples of σ aromatic MH_50+- clusters which may be experimentally viable.

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SUPPLEMENTARY INFORMATION

Table S1 and cartesian coordinates of all the minimum energy structures calculated at TPSSh/def2-TZVP level have been provided as supplementary information appended in the end of article.

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SUPPLEMENTARY INFORMATION

Table S1. Results of different density functionals of D_{5h} symmetric CsF₅ and BaH₅⁺ clusters. Lowest vibrational frequencies (v₁) are in cm⁻¹. Basis set used was def2-TZVP.

Functional↓/Cluster→	CsF5	BaF5 ⁺
	V 1	V 1
TPSSh	525	540
B3LYP-D3(BJ)	509	526
PBE0	566	599
ωB97XD	518	268

Cartesian coordinates of the optimized geometries of the clusters at TPSSh/def2-TZVP level.

NiH5⁻ (D5h)

1	0.370138000	-1.435874000	-0.000443000
1	1.479479000	-0.093923000	0.000849000
1	-1.251839000	-0.795373000	0.000816000
1	-1.142638000	0.944824000	0.000071000
28	-0.000088000	0.000075000	-0.000047000
1	0.547324000	1.378234000	0.000018000
Nil	$H_5^-(C_{2V})$		
1	1.474564000	0.434693000	0.000007000
1	-0.179257000	-1.523410000	-0.000052000
1	-0.176395000	1.523707000	-0.000003000
1	1.474203000	-0.436367000	0.000130000
28	-0.038626000	0.000002000	-0.000009000
1	-1.511590000	0.001320000	0.000171000
Pd	H5 ⁻ (D5h)		
1	0.751118000	-1.420893000	0.000168000
1	1.583880000	0.273594000	-0.000168000
1	-1.120068000	-1.152841000	-0.000190000
1	-1.442620000	0.709381000	0.000054000
46	-0.000052000	-0.000001000	0.000003000
1	0.230088000	1.590803000	0.000017000
Pd	H5 ⁻ (C2v)		
1	-1.597614000	0.009258000	-0.000221000
1	-0.186166000	1.645204000	0.000384000
1	-0.206834000	-1.642939000	0.000124000
1	1.667420000	-0.427799000	0.000429000
46	-0.029255000	0.000002000	-0.000003000
1	1.668925000	0.416183000	-0.000584000

Pu	15° (D5h)		
1	0.924097000	-1.336544000	-0.000267000
1	1.556945000	0.464624000	-0.000193000
1	-0.985889000	-1.291804000	-0.000463000
1	-1.533271000	0.538948000	-0.000071000
78	-0.000020000	0.000004000	0.000019000
1	0.039694000	1.624466000	-0.000509000
PtH	$H_5^-(C_{2V})$		
1	-1.612657000	-0.000700000	-0.000242000
1	-0.200847000	1.647401000	0.000661000
1	-0.199099000	-1.647614000	0.000368000
1	1.616579000	-0.468791000	0.000259000
78	-0.015644000	-0.000003000	-0.000016000
1	1.616269000	0.469935000	0.000187000
Au	H5 (D5h)		
1	0.701177000	-1.452253000	-0.000116000
1	1.598121000	0.215925000	-0.000015000
1	-1.164810000	-1.115423000	0.000260000
1	-1.420692000	0.763667000	-0.000247000
79	-0.000038000	0.000019000	-0.000001000
1	0.289231000	1.586589000	0.000198000
Au	$H_5(C_{2V})$		
1	1.795625000	0.402881000	-0.000047000
1	-0.120720000	-1.635105000	-0.000015000
1 1	-0.120720000 -0.120199000	-1.635105000 1.635146000	-0.000015000 -0.000018000
1 1 1	-0.120720000 -0.120199000 1.795585000	-1.635105000 1.635146000 -0.403186000	-0.000015000 -0.000018000 -0.000075000
1 1 1 79	-0.120720000 -0.120199000 1.795585000 -0.022606000	-1.635105000 1.635146000 -0.403186000 0.000001000	-0.000015000 -0.000018000 -0.000075000 0.000002000
1 1 1 79 1	-0.120720000 -0.120199000 1.795585000 -0.022606000 -1.564404000	-1.635105000 1.635146000 -0.403186000 0.000001000 0.000200000	-0.000015000 -0.000018000 -0.000075000 0.00002000
1 1 79 1 Cs]	-0.120720000 -0.120199000 1.795585000 -0.022606000 -1.564404000 H ₅	-1.635105000 1.635146000 -0.403186000 0.000001000 0.000200000	-0.000015000 -0.000018000 -0.000075000 0.000002000 -0.000017000
1 1 79 1 Cs l 1	-0.120720000 -0.120199000 1.795585000 -0.022606000 -1.564404000 H5 -0.333602000	-1.635105000 1.635146000 -0.403186000 0.000001000 0.000200000	-0.000015000 -0.000018000 -0.000075000 -0.00002000 -0.000017000
1 1 79 1 Cs 1 1	-0.120720000 -0.120199000 1.795585000 -0.022606000 -1.564404000 H5 -0.333602000 -1.928315000	-1.635105000 1.635146000 -0.403186000 0.000001000 0.000200000 -1.918583000 -0.275543000	-0.000015000 -0.000018000 -0.000075000 -0.00002000 -0.000017000 -0.000054000 -0.000038000
1 1 79 1 Cs 1 1 1	-0.120720000 -0.120199000 1.795585000 -0.022606000 -1.564404000 H5 -0.333602000 -1.928315000 1.721587000	-1.635105000 1.635146000 -0.403186000 0.000001000 0.000200000 -1.918583000 -0.275543000 -0.910067000	-0.000015000 -0.000075000 0.000002000 -0.000017000 0.000054000 -0.000038000
1 1 79 1 Cs 1 1 1 1	-0.120720000 -0.120199000 1.795585000 -0.022606000 -1.564404000 H5 -0.333602000 1.928315000 1.721587000 1.397701000	-1.635105000 1.635146000 -0.403186000 0.00001000 0.000200000 -1.918583000 -0.275543000 -0.910067000 1.356197000	-0.000015000 -0.000075000 0.00002000 -0.000017000 0.000054000 -0.000038000 -0.000028000 0.000013000
1 1 79 1 Cs 1 1 1 1 1 55	-0.120720000 -0.120199000 1.795585000 -0.022606000 -1.564404000 H5 -0.333602000 -1.928315000 1.721587000 1.397701000 0.000010000	-1.635105000 1.635146000 -0.403186000 0.00001000 0.000200000 -1.918583000 -0.275543000 -0.910067000 1.356197000 -0.000011000	-0.000015000 -0.000075000 0.00002000 -0.000017000 0.000054000 -0.000038000 0.000013000 -0.00001000
1 1 79 1 Csl 1 1 1 1 55 1	-0.120720000 -0.120199000 1.795585000 -0.022606000 -1.564404000 H5 -0.333602000 1.928315000 1.721587000 1.397701000 0.000010000 -0.857935000	-1.635105000 1.635146000 -0.403186000 0.00001000 0.000200000 -1.918583000 -0.910067000 1.356197000 -0.000011000 1.748587000	-0.00015000 -0.00018000 0.00002000 -0.000017000 -0.000054000 -0.000038000 -0.000028000 0.000013000 -0.00001000
1 1 79 1 Csl 1 1 1 1 55 1 Ba	-0.120720000 -0.120199000 1.795585000 -0.022606000 -1.564404000 H5 -0.333602000 -1.928315000 1.721587000 1.397701000 0.000010000 -0.857935000 H5+	-1.635105000 1.635146000 -0.403186000 0.00001000 0.000200000 -1.918583000 -0.275543000 -0.910067000 1.356197000 -0.000011000 1.748587000	-0.000015000 -0.000075000 0.00002000 -0.000017000 0.000054000 -0.000038000 -0.000028000 0.000013000 0.00001000
1 1 79 1 Csl 1 1 1 1 55 1 Baa 1	-0.120720000 -0.120199000 1.795585000 -0.022606000 -1.564404000 H5 -0.333602000 1.721587000 1.721587000 1.397701000 0.000010000 0.0857935000 H5 ⁺ -0.733876000	-1.635105000 1.635146000 -0.403186000 0.00001000 0.000200000 -1.918583000 -0.910067000 1.356197000 -0.000011000 1.748587000	-0.00015000 -0.000075000 -0.00002000 -0.000017000 -0.000054000 -0.000038000 -0.000028000 -0.00001000 0.000028000
1 1 79 1 Csl 1 1 1 55 1 Bal 1 1	-0.120720000 -0.120199000 1.795585000 -0.022606000 -1.564404000 H5 -0.333602000 -1.928315000 1.721587000 1.397701000 0.000010000 0.857935000 H5 ⁺ -0.733876000 -1.919965000	-1.635105000 1.635146000 0.00001000 0.000200000 -1.918583000 -0.910067000 1.356197000 1.356197000 1.748587000 1.780255000 -0.147868000	-0.00015000 -0.000075000 -0.00002000 -0.000017000 -0.000054000 -0.000038000 -0.000013000 -0.00001000 0.000028000 0.000390000 -0.00028600
1 1 79 1 Csl 1 1 1 1 55 1 Bai 1 1 1	-0.120720000 -0.120199000 1.795585000 -0.022606000 -1.564404000 H5 -0.333602000 1.928315000 1.721587000 1.397701000 0.000010000 0.0857935000 H5 ⁺ -0.733876000 -1.919965000 1.466301000	-1.635105000 1.635146000 -0.403186000 0.00001000 0.000200000 -1.918583000 -0.910067000 1.356197000 1.356197000 1.748587000 1.780255000 -0.147868000 1.247961000	-0.00015000 -0.000075000 -0.00002000 -0.000017000 -0.000054000 -0.000038000 -0.000028000 -0.00001000 0.000028000 -0.00028000 -0.000286000
1 1 79 1 Csl 1 1 1 1 55 1 Ba 1 1 1 1	-0.120720000 -0.120199000 1.795585000 -0.022606000 -1.564404000 H5 -0.333602000 1.721587000 1.397701000 0.000010000 0.857935000 H5 ⁺ -0.733876000 1.466301000 1.639906000	-1.635105000 1.635146000 0.00001000 0.000200000 -1.918583000 -0.275543000 1.356197000 1.356197000 1.748587000 1.748587000 1.780255000 -0.147868000 1.247961000 -1.008675000	-0.00015000 -0.00075000 -0.00002000 -0.00017000 -0.000054000 -0.000038000 -0.000028000 0.000013000 -0.00028000 -0.00028000 -0.00025000
1 1 79 1 Csl 1 1 1 55 1 Bal 1 1 1 1 1 1 1 1 5 5 1 Bal 1 1 1 5 5 1 B 1 1 5 5 1 B 1 5 5 5 1 B 1 5 5 5 B 1 5 5 5 B B B B B B B B	-0.120720000 -0.120199000 1.795585000 -0.022606000 -1.564404000 H5 -0.333602000 1.928315000 1.721587000 1.397701000 0.000010000 0.0857935000 H5+ -0.733876000 1.919965000 1.466301000 1.639906000	-1.635105000 1.635146000 0.00001000 0.000200000 0.000200000 -1.918583000 -0.910067000 1.356197000 1.356197000 1.748587000 1.780255000 -0.147868000 1.247961000 -1.008675000 -0.00007000	-0.00015000 -0.000075000 -0.00002000 -0.000017000 -0.000054000 -0.000038000 -0.000028000 -0.000028000 -0.000028000 -0.000286000 -0.000025000