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Flattening a Puckered Pentasilacyclopentadienide Ring by Suppression of the Pseudo Jahn–Teller Effect

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We report the theoretical prediction of flattening of the puckered Si_5 ring by suppression of the pseudo-Jahn–Teller effect through coordination of two Mg^{2+} cations to the Si_5H_5^- anion to make an inverse $[\text{Mg}^{2+}\text{Si}_5\text{H}_5^-\text{Mg}^{2+}]$ sandwich complex. The pseudo-Jahn–Teller (PJT) effect was suppressed through the OMO–UMO gaps increase in the resultant $[\text{Mg}^{2+}\text{Si}_5\text{H}_5^-\text{Mg}^{2+}]$ sandwich complex, as compared to the initial Si_5H_5^- anion. It was the influence of two Mg^{2+} cations that caused the OMO–UMO gaps increase that made this type of PJT effect suppression work. In the three other complexes under the current computational study, namely, $[\text{Li}^+\text{Si}_5\text{H}_5^-\text{Li}^+]$, $[\text{Na}^+\text{Si}_5\text{H}_5^-\text{Na}^+]$, and $[\text{Be}^{2+}\text{Si}_5\text{H}_5^-\text{Be}^{2+}]$, the Si_5H_5^- moiety remains nonplanar. We believe that if the $\text{Mg}(\text{Si}_5\text{H}_5)_2$ solid compound were synthesized, it could have planar Si_5H_5^- building blocks.

Introduction

Cyclic systems such as benzene (C_6H_6), cyclopentadienyl anion (C_5H_5^-), and the recently synthesized cyclotetrabutadiene dianion derivative $((\text{Me}_3\text{Si})_4\text{C}_4^{2-})^{1-3}$ are planar due to π -aromaticity, since they all have six π -electrons. These three cyclic systems are prototypical aromatic systems according to the $4n + 2$ Hückel rule where $n = 1$. Out of three silicon analogues, only the tetrasiliconcyclobutadiene dianion derivative $[(\text{tBu}_2\text{MeSi})_4\text{Si}_4]^{2-}$, as a part of the $[\text{K}(\text{thf})_2][(\text{tBu}_2\text{MeSi})_4\text{Si}_4]$ salt, was synthesized⁴ and shown to have a planar tetraatomic cyclic structure at the core using X-ray diffraction. The Si_6H_6 and Si_5H_5^- species have not been obtained experimentally yet. Theoretical calculations of Si_6H_6 and Si_5H_5^- showed that both of these molecules are nonplanar.^{5,6} The deviation from planarity in Si_6H_6 and Si_5H_5^- species is caused by the only source of instability of high-symmetry configurations of polyatomic systems, namely, the Jahn–Teller vibronic effects.^{7–9}

the pseudo-Jahn–Teller (PJT) effect to be precise. We have demonstrated recently¹⁰ that the PJT effect can be suppressed by flattening the nonplanar “chair” structure of Si_6X_{12} ($\text{X} = \text{Cl}, \text{Br}$) upon addition of two X^- ions to form the $[\text{Si}_6\text{X}_{14}]^{2-}$ dianion. The resultant $[\text{Si}_6\text{Cl}_{14}]^{2-}$ dianion was shown to have the restored planar Si_6 hexagon ring “sandwiched” between two apical chlorides.¹⁰ The comprehensive computational analysis of the $\text{Si}_6\text{Cl}_{12}$ electronic structure allowed us to identify the main cause of the suppression of the PJT effect, which originates from filling the initially empty unoccupied molecular orbitals (UMOs) of $\text{Si}_6\text{Cl}_{12}$ with electrons of the adduct (i.e., Cl^-). In the current article we show that there is an alternative mechanism of suppression of the PJT effect through extending the gap between interacting occupied and empty MOs, which participate in the PJT effect. We also demonstrate that the Si_5H_5^- structure, which is nonplanar in the isolated state, becomes planar in the $[\text{MgSi}_5\text{H}_5\text{Mg}]^{3+}$ sandwich complex through the OMO–UMO gaps increase caused by positive charge influence of the two extra Mg^{2+} cations.

Computational Results

We initially calculated the planar pentagonal D_{5h} ($^1A_1'$) structure of Si_5H_5^- (Figure 1, structure I) at two levels of theory: B3LYP/6-311++G** and CCSD(T)/6-311++G**.

All calculations were performed using the Gaussian 03 program.¹¹ Geometry and molecular orbital visualization was done using the MOLEKEL 4.3 package.¹² We found that the D_{5h} ($^1A_1'$) structure I is not a minimum, in agreement with the previously reported computational results for Si_5H_5^- by Korkin et al.⁶ It was found to have two doubly degenerate imaginary frequencies ($\omega_{1,2}(\text{e}_2'')$ and $\omega_{3,4}(\text{e}_1'')$), leading to out-of-plane distortions, according to the B3LYP/6-311++G** and the CCSD(T)/6-311++G** levels of theory. Geometry optimization (at B3LYP/6-311++G**) following these imaginary frequency modes leads

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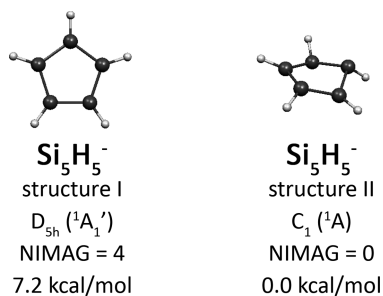


Figure 1. Alternative structures of Si_5H_5^- (structure I and structure II), their symmetry, spectroscopic states, number of imaginary frequency modes (NIMAG), and relative energies corrected for zero-point energy, all calculated at the B3LYP/6-311++G** level of theory.

to one isomer: $C_1 (^1A)$ (Figure 1, structure II). We also repeated geometry optimization for the two isomers, which were previously reported by Korkin et al.⁶ The authors found two degenerate nonplanar isomers of Si_5H_5^- of C_s and C_2 symmetry, respectively, according to their calculations performed at the MP2(full)/6-31G* level of theory. We found that these two isomers reported by Korkin et al. are not minima at the B3LYP/6-311++G** level of theory, which is used in the current work. Geometry optimization following imaginary frequency modes of C_s and C_2 isomers leads again to structure II. Hence, there is only one isomer of Si_5H_5^- at B3LYP/6-311++G**, which is of C_1 symmetry in the 1A electronic state (Figure 1, structure II). The planar $D_{5h} (^1A_1')$ structure I is only 7.2 kcal/mol higher in energy than the puckered $C_1 (^1A)$ structure II at the B3LYP/6-311++G** level of theory with zero-point energy correction.

The planar $D_{5h} (^1A_1')$ structure I is not a minimum due to the pseudo-Jahn–Teller (PJT) effect, which forces puckering of the Si_5 ring and leads to out-of-plane distortions along the imaginary frequency modes. The PJT effect in the $D_{5h} (^1A_1')$, $1a_1'^2 1e_1'^4 1e_2'^4 2a_1'^2 2e_1'^4 2e_2'^4 1a_2'^2 1e_1'^0 3a_1'^0 3e_1'^0 3e_2'^0$ structure of Si_5H_5^- is a consequence of vibronic coupling of pairs of occupied molecular orbitals (OMO) and unoccupied molecular orbitals (UMO). The symmetry rule for the PJT effect is that the symmetry of the reaction coordinate (symmetry of one of the two doubly degenerate imaginary frequency modes) should be the same as the direct product of the OMO and UMO states¹³ as follows (eq 1):

$$\psi_{\text{OMO}} \times \psi_{\text{UMO}} = \Gamma_{\text{RctnCoord}} \quad (1)$$

Thus, the deformation of the $D_{5h} (^1A_1')$ structure I of Si_5H_5^- along the $\omega_{1,2}(e_2'')$ imaginary frequency mode can be caused by interaction between the HOMO ($1e_1''$) and LUMO+1 ($3e_1'$) (see eq 2 and Figure 2a) and/or by interaction between the HOMO ($1e_1''$) and LUMO+2 ($3e_2'$) (see eq 3 and Figure 2b):

$$e_1'' \times e_1' = a_1'' + a_2'' + e_2'' \quad (2)$$

$$e_1'' \times e_2' = e_1'' + e_2'' \quad (3)$$

The deformation of the $D_{5h} (^1A_1')$ structure I of Si_5H_5^- along the $\omega_{3,4}(e_1'')$ imaginary frequency mode can be caused by interaction between the HOMO ($1e_1''$) and LUMO ($3a_1'$) (see eq 4 and Figure 2c) and/or by interaction between the HOMO ($1e_1''$) and LUMO+2 ($3e_2'$) (see eq 3 and Figure 2b):

$$e_1'' \times a_1' = e_1'' \quad (4)$$

The orbital energies of the orbitals involved in the pseudo-Jahn–Teller effect are the following: $\epsilon(\text{HOMO}, 1e_1'') = -0.078$ au; $\epsilon(\text{LUMO}, 3a_1') = 0.164$ au; $\epsilon(\text{LUMO}+1, 3e_1') = 0.165$ au; and $\epsilon(\text{LUMO}+2, 3e_2') = 0.172$ au. Thus, the orbital energy difference

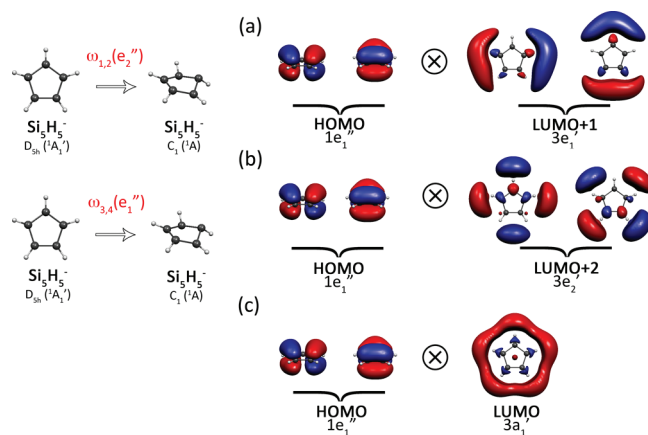


Figure 2. Interaction of the pairs of occupied and unoccupied molecular orbitals of the $D_{5h} (^1A_1')$ structure I of Si_5H_5^- responsible for the PJT effect: (a) and (b) interactions cause distortion toward the $C_1 (^1A)$ structure upon following the doubly degenerate $\omega_{1,2}(e_2'')$ imaginary frequency mode; (b) and (c) interactions cause distortion toward the $C_1 (^1A)$ structure upon following the doubly degenerate $\omega_{3,4}(e_1'')$ imaginary frequency mode.

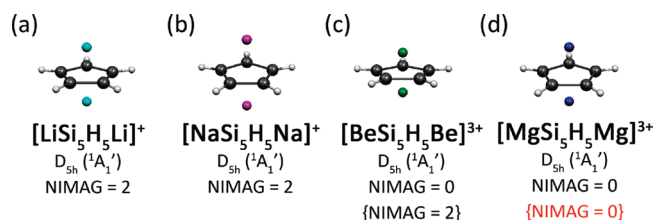


Figure 3. Optimized structures, point group symmetry, spectroscopic states, and number of imaginary frequency modes (NIMAG) of (a) $\text{Li}^+\text{Si}_5\text{H}_5^-\text{Li}^+$, (b) $\text{Na}^+\text{Si}_5\text{H}_5^-\text{Na}^+$, (c) $\text{Be}^{2+}\text{Si}_5\text{H}_5^-\text{Be}^{2+}$, and (d) $\text{Mg}^{2+}\text{Si}_5\text{H}_5^-\text{Mg}^{2+}$ at the B3LYP/6-311++G** level of theory and at the CCSD(T)/6-311++G** level of theory (in curly brackets).

in the Si_5H_5^- anion between the HOMO and LUMO is 6.58 eV, while the gap between the HOMO and LUMO+1 is 6.60 eV, which are both somewhat smaller than the energy difference between the HOMO and LUMO+2 (6.80 eV). All the above values are given at the RHF/6-311++G** level of theory since our most reliable data were obtained at the CCSD(T)/6-311++G** level, which is based on RHF/6-311++G**.

In order to test if the PJT effect can be suppressed by external charges, we then calculated four inverse sandwich complexes, namely, $\text{Li}^+\text{Si}_5\text{H}_5^-\text{Li}^+$ (Figure 3a), $\text{Na}^+\text{Si}_5\text{H}_5^-\text{Na}^+$ (Figure 3b), $\text{Be}^{2+}\text{Si}_5\text{H}_5^-\text{Be}^{2+}$ (Figure 3c), and $\text{Mg}^{2+}\text{Si}_5\text{H}_5^-\text{Mg}^{2+}$ (Figure 3d) at the B3LYP/6-311++G** level of theory.

In the following text are the results of testing whether the electrostatic field from the pair of Li^+ , Na^+ , Be^{2+} , or Mg^{2+} cations is enough to suppress the PJT effect in the Si_5H_5^- anion by shifting apart occupied molecular orbitals (OMO) and unoccupied molecular orbitals (UMO). The addition of two Li^+ or Na^+ cations to make the $\text{M}^+\text{Si}_5\text{H}_5^-\text{M}^+$ ($\text{M} = \text{Li}, \text{Na}$) complex or a pair of Be^{2+} or Mg^{2+} dications to make $\text{M}^{2+}\text{Si}_5\text{H}_5^-\text{M}^{2+}$ ($\text{M} = \text{Be}, \text{Mg}$) does not increase the number of valence electrons in the resultant inverse sandwich complex, as compared to the initial Si_5H_5^- anion, although this coordination of the two positively charged ions to Si_5H_5^- affects the gap between occupied and unoccupied molecular orbitals responsible for the PJT effect, which manifests itself in the increased stability of the $\text{M}^{n+}\text{Si}_5\text{H}_5^-\text{M}^{n+}$ complexes. According to our calculations, all four complexes shown in Figure 3 do not have doubly degenerate

imaginary frequency mode of e_1'' symmetry, which was present in isolated Si_5H_5^- . That's due to the gap increase between pairs of OMO-UMO molecular orbitals: $1e_1''$ and $3a_1'$; $1e_1''$ and $3e_2'$. The gap between $1e_1''$ and $3a_1'$ OMO-UMO pair is increased from 6.58 eV to 8.18 eV (in $\text{Li}^+\text{Si}_5\text{H}_5^-$); from 6.58 eV to 7.27 eV (in $\text{Na}^+\text{Si}_5\text{H}_5^-$); from 6.58 eV to 9.15 eV (in $\text{Be}^{2+}\text{Si}_5\text{H}_5^-$); and from 6.58 eV to 7.16 eV (in $\text{Mg}^{2+}\text{Si}_5\text{H}_5^-$). The gap between $1e_1''$ and $3e_2'$ OMO-UMO pair is increased from 6.80 eV to 9.95 eV (in $\text{Li}^+\text{Si}_5\text{H}_5^-$); from 6.80 eV to 9.42 eV (in $\text{Na}^+\text{Si}_5\text{H}_5^-$); from 6.80 eV to 11.99 eV (in $\text{Be}^{2+}\text{Si}_5\text{H}_5^-$); and from 6.80 eV to 10.94 eV (in $\text{Mg}^{2+}\text{Si}_5\text{H}_5^-$). Apparently, these gaps' increase was enough to completely suppress the PJT effect along the $\omega_{3,4}(e_1'')$ mode. However, two complexes, $\text{Li}^+\text{Si}_5\text{H}_5^-$ and $\text{Na}^+\text{Si}_5\text{H}_5^-$, retained doubly degenerate imaginary frequency mode of e_2'' symmetry upon addition of cations to isolated Si_5H_5^- . Thus, the presence of two extra Li^+ or Na^+ cations does not suppress the PJT effect completely, although it reduces the number of degenerate imaginary frequency modes by one. Both $\text{Be}^{2+}\text{Si}_5\text{H}_5^-$ and $\text{Mg}^{2+}\text{Si}_5\text{H}_5^-$ complexes were found to be minima at the B3LYP/6-311++G** level of theory. However, when we reoptimized the geometry of the $\text{Be}^{2+}\text{Si}_5\text{H}_5^-$ complex and calculated its frequency modes at the CCSD(T)/6-311++G** level of theory, it was found to have one doubly degenerate imaginary frequency of e_2'' symmetry. Thus, Be^{2+} cations cannot suppress the PJT effect either. Meanwhile, the $\text{Mg}^{2+}\text{Si}_5\text{H}_5^-$ complex was found to be a minimum at both levels of theory, with the lowest $\omega_{1,2}(e_2'')$ frequency mode being 90.0 cm^{-1} (B3LYP/6-311++G**) and 78.8 cm^{-1} (CCSD(T)/6-311++G**), which indicates that only the electrostatic field of Mg^{2+} causes the suppression of the PJT effect. The orbital energies of the orbitals of $\text{Mg}^{2+}\text{Si}_5\text{H}_5^-$, which correspond to those involved in pseudo-Jahn–Teller effect of Si_5H_5^- , are the following: $\epsilon(\text{HOMO}, 1e_1'') = -0.737\text{ au}$; $\epsilon(\text{LUMO}, 3a_1') = -0.474\text{ au}$; $\epsilon(\text{LUMO}+4, 3e_1') = -0.350\text{ au}$; and $\epsilon(\text{LUMO}+5, 3e_2') = -0.335\text{ au}$. Hence, the gap between the HOMO ($1e_1''$) and LUMO ($3a_1'$) is increased from 6.58 eV in Si_5H_5^- to 7.16 eV in $\text{Mg}^{2+}\text{Si}_5\text{H}_5^-$. The gaps between other UMO and OMO pairs that participate in the PJT effect are increased by more than 0.60 eV in $\text{Mg}^{2+}\text{Si}_5\text{H}_5^-$: from 6.60 eV to 10.52 eV (in the case of $1e_1''$ and $3e_1'$) and from 6.80 eV to 10.94 eV (in the case of $1e_1''$ and $3e_2'$). Apparently this extension of UMO–OMO gaps is large enough to attain planarity of Si_5H_5^- in the inverse sandwich structure of $\text{Mg}^{2+}\text{Si}_5\text{H}_5^-$. As one of the reviewers recommended, we performed additional calculations at B3LYP/6-311++G** to study the planarity or lack of planarity of the underlying five-membered ring in $\text{Mg}^{2+}\text{Si}_5\text{H}_5^-$ as the distance between the magnesium cations and the ring is varied. We performed frequency calculations of $\text{Mg}^{2+}\text{Si}_5\text{H}_5^-$ at longer (with two Mg^{2+} cations moved farther from the center of mass by 0.1 Å) and shorter (with two Mg^{2+} cations moved closer to the center of mass by 0.1 Å) cation–ring distances, as well as with one Mg^{2+} cation moved farther from the center of mass by 0.1 Å and the other Mg^{2+} cation moved closer to the center of mass by 0.1 Å. In the two latter cases the $\text{Mg}^{2+}\text{Si}_5\text{H}_5^-$ retained no imaginary frequencies, while the $\text{Mg}^{2+}\text{Si}_5\text{H}_5^-$ with longer cation–ring distances has two imaginary frequencies. This elucidates the fact that the cation–ring interactions are mainly Coulombic and that there is a delicate balance between external field of cations and the geometry.

One would expect that Be^{2+} cation being smaller and hence located closer to the Si_5H_5^- ring should also form the stable $\text{M}^{2+}\text{Si}_5\text{H}_5^-$ complex similar to $\text{Mg}^{2+}\text{Si}_5\text{H}_5^-$. Indeed, the gap between $1e_1''$ and $3e_1'$ pair of OMO-UMO molecular orbitals (involved in PJT effect along the doubly degenerate imaginary frequency mode of e_2'' symmetry) is increased from 6.60 eV (in Si_5H_5^-) to 11.56 eV (in $\text{Be}^{2+}\text{Si}_5\text{H}_5^-$), hence, by 4.96 eV. This gap increase in $\text{Be}^{2+}\text{Si}_5\text{H}_5^-$ is even higher than there in $\text{Mg}^{2+}\text{Si}_5\text{H}_5^-$ (which is 3.72 eV). We believe, that the suppression of the PJT distortion in $\text{Be}^{2+}\text{Si}_5\text{H}_5^-$

doesn't occur due to the nature of chemical bonding. Natural Bonding Orbital atomic charges calculated at B3LYP/6-311++G** are +1.30 |e| on each of the beryllium atoms and +0.40 |e| on Si_5H_5 ring in $\text{Be}^{2+}\text{Si}_5\text{H}_5^-$, while in the $\text{Mg}^{2+}\text{Si}_5\text{H}_5^-$ complex they are +1.65 |e| on each of the magnesium atoms and −0.30 |e| on Si_5H_5 ring. This elucidates that the nature of the chemical bonding in the $\text{Be}^{2+}\text{Si}_5\text{H}_5^-$ complex is more covalent than there in the $\text{Mg}^{2+}\text{Si}_5\text{H}_5^-$ complex. The $\text{Li}^+\text{Si}_5\text{H}_5^-$ and $\text{Na}^+\text{Si}_5\text{H}_5^-$ complexes are more ionic as expected: the natural charges in $\text{Li}^+\text{Si}_5\text{H}_5^-$ are +0.87 |e| (on each of the lithium atoms) and −0.74 |e| (on Si_5H_5 ring); and there in the $\text{Na}^+\text{Si}_5\text{H}_5^-$ complex they are +0.93 |e| (on each of the sodium atoms) and −0.86 |e| (on Si_5H_5 ring). The electrostatic field of a singly charged cation is weaker than that of doubly charged one. The gap between $1e_1''$ and $3e_1'$ OMO-UMO pair is increased by 2.85 eV (in $\text{Li}^+\text{Si}_5\text{H}_5^-$), by 2.00 eV (in $\text{Na}^+\text{Si}_5\text{H}_5^-$), as compared to 3.72 eV (in $\text{Mg}^{2+}\text{Si}_5\text{H}_5^-$). This explains why two Li^+ cations or two Na^+ cations cannot suppress the PJT effect in Si_5H_5^- .

The PJT effect is a qualitative model of chemical bonding, and it is not capable of predicting to what extent the OMO–UMO gaps should be increased in order to suppress its distortive nature. However, it can provide direction in the search for the species where the high symmetry can be attained. In our case we studied four types of counter cations, and it was enough to find the appropriate combination of cations to suppress the PJT effect.

Aromaticity in Si_5H_5^- and $\text{Mg}^{2+}\text{Si}_5\text{H}_5^-$

The Si_5H_5^- anion is aromatic in the planar form according to the molecular orbital chemical bonding analysis and the Si–Si bond equalization. We performed a nuclear-independent chemical shift (NICS) analysis¹⁴ for both Si_5H_5^- and its planar carbon analogue, C_5H_5^- . The calculated NICS_{zz} values of the Si_5H_5^- anion were found to be −11.5 ppm ($Z = 0.0\text{ Å}$, where Z represents the distance from the center of the Si_5H_5^- moiety along the z axis), −12.1 ppm ($Z = 0.2\text{ Å}$), −13.5 ppm ($Z = 0.4\text{ Å}$), −15.6 ppm ($Z = 0.6\text{ Å}$), −17.7 ppm ($Z = 0.8\text{ Å}$), and −19.3 ppm ($Z = 1.0\text{ Å}$) at the optimized planar B3LYP/6-311++G** geometry. The above NICS_{zz} values of the Si_5H_5^- anion can be compared to those of the C_5H_5^- anion at the same level of theory: −16.2 ppm ($Z = 0.0\text{ Å}$, where Z represents the distance from the center of the C_5H_5^- moiety along the z axis), −18.7 ppm ($Z = 0.2\text{ Å}$), −24.6 ppm ($Z = 0.4\text{ Å}$), −30.3 ppm ($Z = 0.6\text{ Å}$), −33.5 ppm ($Z = 0.8\text{ Å}$), and −33.7 ppm ($Z = 1.0\text{ Å}$). It is clear that Si_5H_5^- is less aromatic than C_5H_5^- , according to the calculated NICS_{zz} values. Since, the global minimum structure of the Si_5H_5^- anion is nonplanar, the PJT effect overwhelms the stabilization due to aromaticity. When the planarity of the Si_5H_5^- anion is restored in the sandwich $\text{Mg}^{2+}\text{Si}_5\text{H}_5^-$ structure, aromaticity in the Si_5H_5^- anion as a part of the inverse sandwich complex is also restored. The NICS_{zz} values calculated for the $\text{Mg}^{2+}\text{Si}_5\text{H}_5^-$ complex are −15.1 ppm ($Z = 0.0\text{ Å}$), −15.9 ppm ($Z = 0.2\text{ Å}$), −18.2 ppm ($Z = 0.4\text{ Å}$), −21.7 ppm ($Z = 0.6\text{ Å}$), −26.3 ppm ($Z = 0.8\text{ Å}$), and −32.1 ppm ($Z = 1.0\text{ Å}$).

Conclusions

In this article we have shown that the nonplanarity of Si_5H_5^- caused by the pseudo-Jahn–Teller effect can be eliminated through coordination of two Mg^{2+} cations to it to make the

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$\text{Mg}^{2+}\text{Si}_5\text{H}_5^-\text{Mg}^{2+}$ inverse sandwich complex. The PJT effect was suppressed in the Si_5H_5^- anion through the OMO–UMO gaps increase in the $\text{Mg}^{2+}\text{Si}_5\text{H}_5^-\text{Mg}^{2+}$ complex because of the charge influence of two Mg^{2+} cations. We also presented the data on the $[\text{Li}^+\text{Si}_5\text{H}_5^-\text{Li}^+]$, $[\text{Na}^+\text{Si}_5\text{H}_5^-\text{Na}^+]$, and $[\text{Be}^{2+}\text{Si}_5\text{H}_5^-\text{Be}^{2+}]$ complexes. None of them was shown to contain a planar Si_5H_5^- moiety. It was concluded that out of all the studied cations only two Mg^{2+} ions are able to increase the OMO–UMO gaps to an appreciable extent to suppress the PJT effect and restore the planarity of Si_5H_5^- . We believe that suppressing the PJT effect through coordination of extra cations can be a useful tool in restoring high-symmetry structures of numerous molecular species with otherwise distorted cyclic geometries.

The salts containing C_5H_5^- anions are known to form stacking structures, where C_5H_5^- anions together with counterions form “infinite” piles of sandwich-type structures.¹⁵ We hope that our theoretical prediction of planarization of the Si_5H_5^- anion in the $\text{Mg}^{2+}\text{Si}_5\text{H}_5^-\text{Mg}^{2+}$ complex stimulates

the synthesis of the first compounds containing the planar Si_5H_5^- anion.

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Supporting Information Available: Reference 11 in full and Cartesian coordinates of Si_5H_5^- structures as well as those of the $\text{Li}^+\text{Si}_5\text{H}_5^-\text{Li}^+$, $\text{Na}^+\text{Si}_5\text{H}_5^-\text{Na}^+$, $\text{Be}^{2+}\text{Si}_5\text{H}_5^-\text{Be}^{2+}$, and $\text{Mg}^{2+}\text{Si}_5\text{H}_5^-\text{Mg}^{2+}$ complexes are available free of charge via the Internet at <http://pubs.acs.org>.

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