Theoretical Study of Metal−Ligand Bonds in Pb(II) Porphyrins

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The electronic structure of Pb(II) porphyrin (PbP) has been studied by performing ab initio calculations based on a density functional theory. The calculated optimum structure of PbP reasonably agrees with that determined by the X-ray structure analysis. The analysis of the Kohn−Sham orbitals of PbP has revealed that the bond between Pb and the porphyrin ring (Pb−P bond) is mainly constructed from $6p_z$ and 7s orbitals of Pb and $2p_x$ and $2p_y$ orbitals of the four nitrogen atoms. It has also been demonstrated that a Lewis base, CH_3^-, adds to Pb by attacking the unoccupied Pb−P antibonding orbital, which is a counterpart of the Pb−P bonding orbital mentioned above. This mechanism can be also applied to another Group 14 metalloporphyrin and Lewis base bond.

1. Introduction

In the realms of coordination chemistry, various types of transition metal complexes have been studied extensively. In general, transition metal complexes exhibit interesting chemico-physical properties such as structure, optical spectrum, and magnetism. These properties are strongly related to partly filled d or f orbitals of the central transition metal and explained excellently in terms of ligand field theory.[1] On the other hand, relatively less studies on s and p block (nontransition) metal complexes have been made both experimentally and theoretically. Differently from transition metal complexes, nontransition metal ones show less interesting chemico-physical properties owing to fully filled d orbitals. Furthermore, transition metal complexes have common types of structure with specific coordination number, whereas nontransition metal complexes take various coordination numbers and in fact show diverse structures. The diversity of structures in nontransition metal complexes is also ascribed to the fact that d atomic orbitals of the center metal are fully occupied. However, nontransition metal complexes have valence s and p electrons which would play an important role in determining their molecular structures and even in reactivity between metals and ligands.

Shimoni-Livny et al. investigated a close relation between the role of a lone pair of Pb(II) and coordination geometry for a number of Pb(II) complexes.[2] According to their ab initio calculations, the lone pair orbital in Pb(II) complexes with low (2−5) coordination numbers has p character and thus the ligands tend to bond to the Pb atom apart from the lone pair. This is understood qualitatively in terms of a valence shell electron pair repulsion (VSEPR) theory.[1]

Although Shimoni-Livny et al. referred to only the role of the lone pair in determining coordination geometry, the presence of lone pair orbital with p character might affect reactivity of such complexes. Very recently, Nishizakura et al. synthesized a bimetallic four-coordination Pb(II) porphyrin complex in order to investigate roles of the lone pair of the Pb(II) complex in reactivity.[3] Four-coordination Pb(II) porphyrins have already been found to be nonplanar rigid structure where the center metal

is out of plane of the porphyrin ring.[4,5] As intuitively speculated on the basis of the structure and also according to the analysis by Shimoni-Livny et al.,[2] the lone pair orbital of Pb might have p character and present opposite to the porphyrin ring. In contrast to the speculation, Nishizakura et al. found no evidence that Pb has such lone pair orbital.

Guilard et al. synthesized bimetallic metal−metal bonded porphyrins, PMM′L, where P is a porphyrin, M is a group 13 or 14 metal, and M′L is a metal M′ with ligands L.[6−12] Although they did not analyze details of the metal−metal bond, the bimetallic bond implies that the lone pair orbital with p character would not present on the center metal M.

To understand these experimental results, detailed electronic structure calculations of s and p block metal complexes, in particular metalloporphyrins, are necessary. However, there is few ab initio calculations of, for example, Pb(II) and Sn(II) porphyrins. Schaffer and Gouterman carried out electronic structure calculations of Pb(II) and Sn(II) porphyrins by using an extended Hückel method.[13] Although they made a molecular orbital analysis of metal−ligand bonds to some extent, the electronic structure properties were not clarified in detail. Therefore, in this article, we carry out density functional calculations of group 14 metal porphyrins, Pb and Sn porphyrins (PbP and SnP), and analyze their electronic properties. A special emphasis is placed on a detailed description of the metal−ligand bonds of PbP and SnP.

This paper is organized as follows. In the next section, we define a theoretical model mimicking real porphyrin complexes. The method of the present calculations is also described in this section. In section 3, we analyze the calculated results. Finally, the concluding remarks are given in section 4.

2. Method of Calculation

Let us first define a model system employed in the present calculations. The porphyrin ring is mimicked by a free-base porphyrin with no side branches, and its molecular formula is $C_{20}N_4H_{12}$. It is reasonable to assume that the side branches have a minor effect on the nature of the metal−ligand bond. Then, the porphyrin ring is planar structure with D_{4h} symmetry and set on *xy* plane. According to the structure specified by the X-ray structure analysis,[4] a nonplanar structure was adopted as initial

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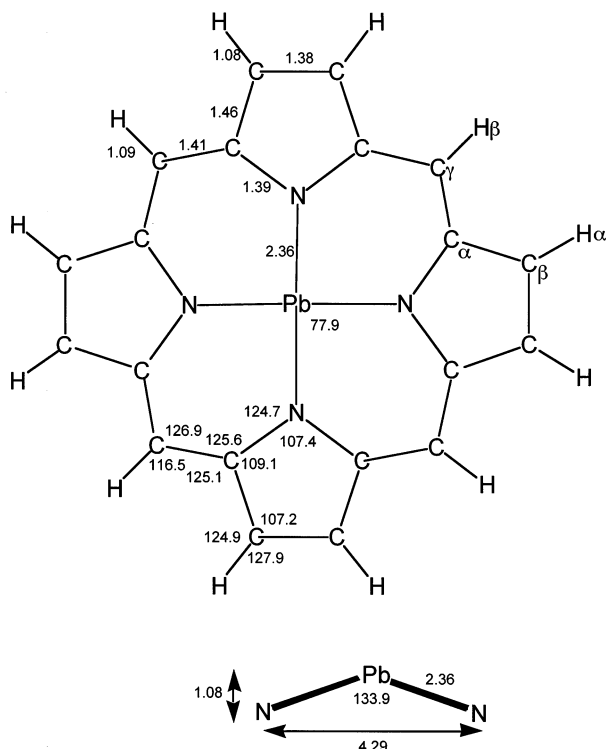
Figure 1. Structural parameters of the optimum geometry of PbP. The bond length and the bond angle are indicated in the units of angstroms and degrees, respectively.

TABLE 1: Atomic Coordinates of PbP

atom[a]	x (Å)	y (Å)	z (Å)
Pb	0.00	0.00	0.86
N	2.09	0.00	−0.21
C_α	2.90	1.12	−0.38
C_β	4.28	0.69	−0.61
C_γ	2.46	2.46	−0.39
H_α	5.11	1.35	−0.77
H_β	3.22	3.22	−0.52

[a] On the Greek alphabet, α, β, and γ, see Figure 1.

geometry of Pb(II) porphyrin, where Pb is out of the *xy* plane by 1.0 Å. This nonplanarity breaks the molecular symmetry from D_{4h} down to C_{4v}. Thus, all of the calculations in this article are performed assuming the C_{4v} molecular symmetry unless otherwise stated.

The electronic structure calculations were based on the Kohn−Sham density functional theory (KS-DFT) with Becke's three-parameter hybrid functional (B3LYP).[14] The LanL2DZ basis set was employed for all elements.[15−18] All of the ab initio calculations were performed by using the Gaussian 98 package of programs.[19]

3. Results and Discussion

3.1. Optimum Geometry and Electronic Structure of Pb(II) Porphyrin. The optimized molecular structure of PbP is shown in Figure 1. The bond length and the bond angle are indicated in the units of angstroms and degrees, respectively. Atomic coordinates of PbP are listed in Table 1. Differently from most four-coordination metalloporphyrins, PbP has a nonplanar square-pyramidal structure. The lead atom lies 1.08 Å out of plane of the four nitrogen atoms. The calculated molecular structure reasonably agrees with that determined by the X-ray structure analysis.[4]

As mentioned in the beginning of this article, the valence s and p electrons of Pb would play an important role in
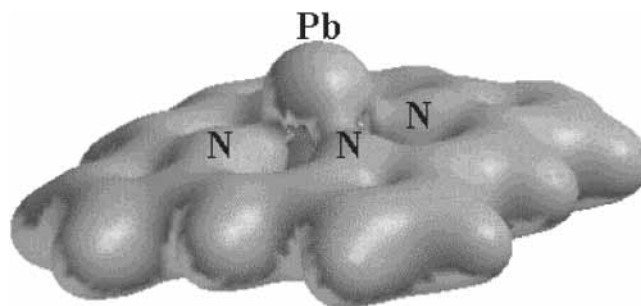

Figure 2. Electric charge density of PbP.

determining molecular structure and also reactivity of the complex. The map of the charge density of PbP shown in Figure 2 reveals that the lone pair electrons are found to distribute spherically around Pb and have no p atomic orbital character which was observed commonly in the non-porphyrin Pb(II) complexes with low coordination numbers.[2] To get a deeper insight into the metal−ligand bond, we analyze the KS orbitals in detail. Figure 3 (left-hand side) shows an energy diagram of the KS orbitals of PbP. The orbital representing the metal-porphyrin (Pb−P) bond corresponds to the third one from the highest occupied molecular orbital (HOMO). This orbital is mainly constructed from the 7s and $6p_z$ orbitals of Pb and the $2p_x$ and $2p_y$ orbitals of the four nitrogen atoms. On the other hand, the lone pair electrons of Pb remain on the metal and occupy mainly the 6s orbital of Pb. The corresponding KS orbital is numbered as 76 in the energy diagram. The formation of the Pb−P bond is depicted schematically in Figure 4. Because the ion radius of Pb^{2+} is larger than those of center metals in other usual metalloporphyrins,[20−25] the Pb−P bond does not form in the *xy* plane. Instead, the unoccupied orbital constructed from the 7s and $6p_z$ atomic Pb orbitals overlaps effectively with the $2p_x$ and $2p_y$ orbitals corresponding to the lone pairs on the four nitrogens. As a result, the Pb−P bonding orbital is formed. The $6s^2$ lone pair orbital of Pb does not contribute to the Pb−P bond formation and remains almost unchanged. As shown in Figure 4, an antibonding orbital is formed as the byproduct of the Pb−P bond formation. This antibonding orbital spreads out opposite to the porphyrin ring. The presence of such a orbital implies the possibility that a Lewis base adds to the center atom in the Pb(II) porphyrins. This is rather unusual compared with other non-porphyrin Pb(II) complexes with low coordination number.[2] To confirm whether a Lewis base adds to the center metal in PbP, we have performed geometry optimization of a system of $CH_3{}^−$−PbP (MePbP$^−$) under the condition of C_s molecular symmetry. The methyl anion was chosen as an example of strong Lewis bases. The geometry optimization has been achieved easily and the total energy of MePbP$^−$ becomes 2.75 eV lower than the sum total of the energies of $CH_3{}^−$ and PbP. It should be noted that the sum total of the zero-point energies of MePbP$^−$ is 0.01 eV higher than that of PbP and $CH_3{}^−$. Thus, the zero-point energy correction is negligible. Structural parameters of the optimum geometry of MePbP$^−$ is shown in Figure 5 and Table 2. The energy levels of the KS orbitals of MePbP$^−$ are shown in Figure 3 (right-hand side). To distinguish the KS orbitals of PbP and MePbP$^−$, the orbitals of MePbP$^−$ are numbered with a prime. Although the ligand $CH_3{}^−$ disturbs the optimum geometry of PbP, the change from fore-optimized structure of PbP is rather minor. In fact, we can reasonably correlate the corresponding KS orbitals of PbP and MePbP$^−$ with each other as shown in Figure 3. For the sake of clear correspondence, we shift the KS orbitals of MePbP$^−$ such that the KS orbital (86′) coincides with

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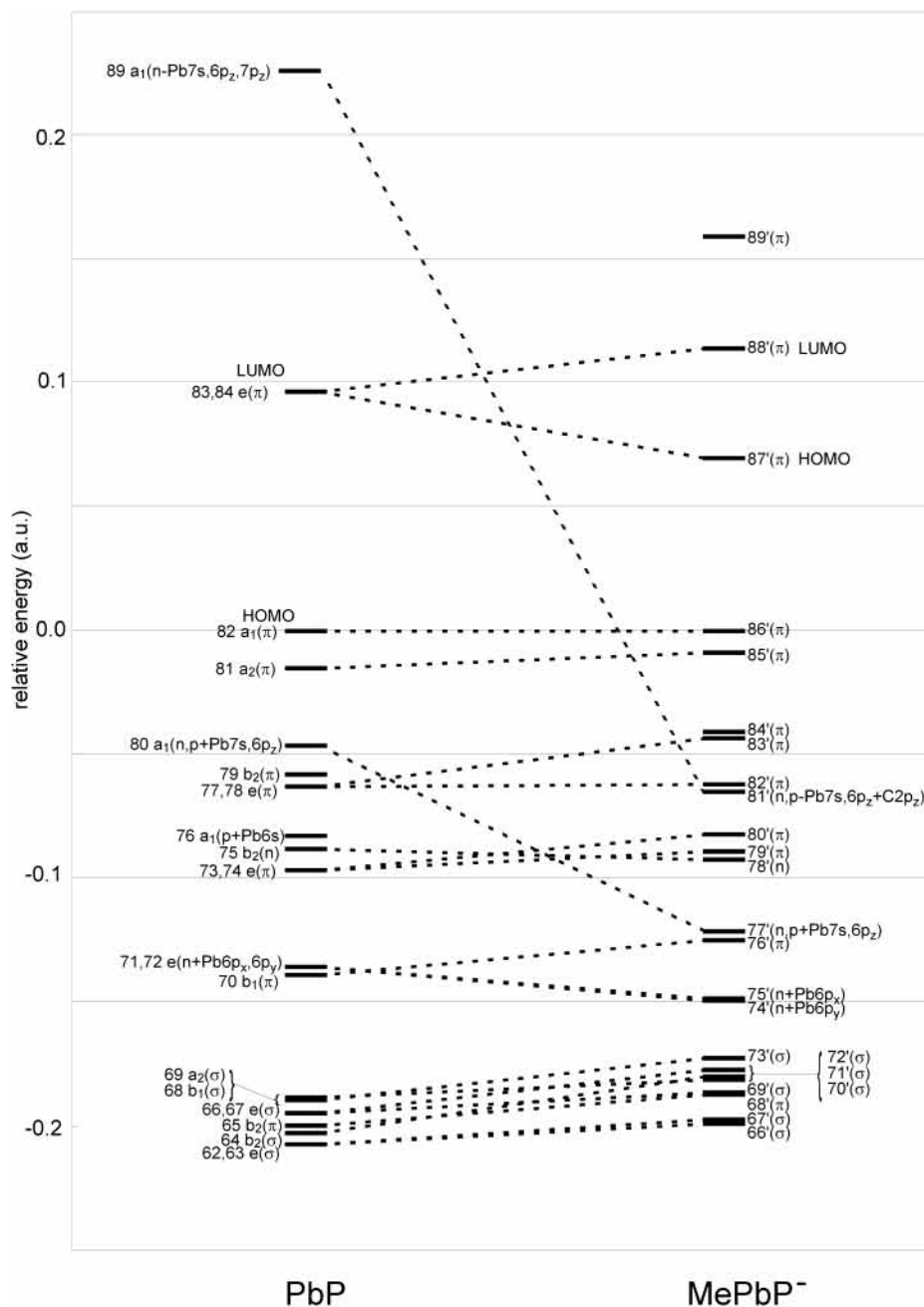*J. Phys. Chem. A, Vol. 107, No. 13, 2003* **2353**

Figure 3. Energy diagrams of the Kohn−Sham orbitals of PbP and MePbP⁻. Corresponding orbitals are correlated with each other. The orbitals are numbered in order of the orbital energy. In the diagram, n denotes lone pairs of four nitrogen atoms, and σ and π denote σ and π bonds in the porphyrin flame, respectively.
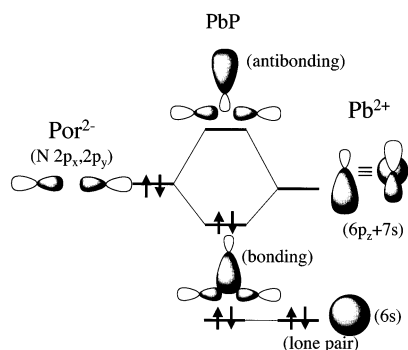

Figure 4. Schematic diagram of the Pb−P bond formation in PbP.

the HOMO orbital of PbP. There are two characteristic KS orbitals of MePbP⁻ to be discussed; the orbitals numbered as

77′ and 81′. The former orbital corresponds to the Pb−P bonding orbital in MePbP⁻, and the latter one represents the bonding orbital between Pb and CH₃⁻ (Pb−C bond). Let us first consider the Pb−C bond formation. The formation of the Pb−C bonding orbital is depicted schematically in Figure 6. The $6p_z$ and $7s$ orbitals of Pb form the Pb−P antibonding orbital which is virtually constructed as a counterpart of the Pb−P bonding orbital described above. (See, the antibonding orbital labeled as 89 of PbP.) This antibonding orbital and the $2p_z$ orbital of C form the Pb−C bonding orbital.

Although the Pb−C bonding orbital makes use of the Pb−P antibonding orbital as mentioned above, the Pb−P bond is energetically stabilized significantly in MePbP⁻ (see, 80 and 77′ KS orbitals). When the Lewis base adds to the center metal of PbP, the electric charge density is much more biased toward the porphyrin ring. This is because the porphyrin ring serves as
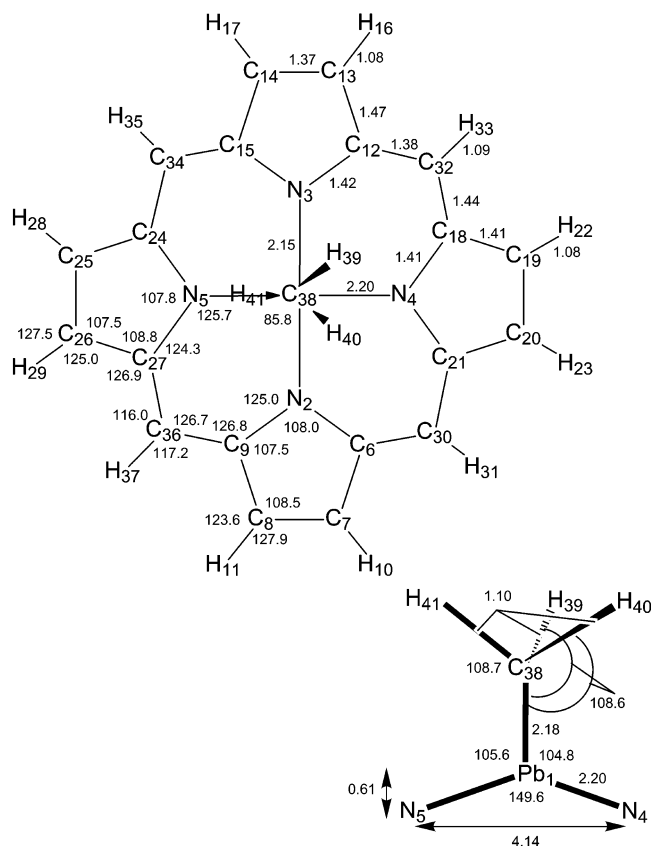
Figure 5. Same as Figure 1 but for MePbP⁻.

Figure 6. Schematic diagram of the bond formation between an additional ligand (Lewis base, CH_3^-) and Pb in MePbP⁻.

Figure 7. Same as Figure 1 but for FeSnP.

TABLE 2: Atomic Coordinates of MePbP⁻

atom[a]	x (Å)	y (Å)	z (Å)	atom[a]	x (Å)	y (Å)	z (Å)
Pb$_1$	0.00	0.00	0.36	H$_{22}$	5.14	1.37	−0.54
N$_2$	0.00	−2.07	−0.25	H$_{23}$	5.14	−1.37	−0.54
N$_3$	0.00	2.07	−0.25	C$_{24}$	−2.95	1.14	−0.31
N$_4$	2.12	0.00	−0.22	C$_{25}$	−4.29	0.71	−0.43
N$_5$	−2.12	0.00	−0.22	C$_{26}$	−4.29	−0.71	−0.43
C$_6$	1.15	−2.90	−0.30	C$_{27}$	−2.95	−1.14	−0.31
C$_7$	0.68	−4.29	−0.37	H$_{28}$	−5.14	1.37	−0.53
C$_8$	−0.699	−4.29	−0.37	H$_{29}$	−5.14	−1.37	−0.53
C$_9$	−1.15	−2.90	−0.30	C$_{30}$	2.46	−2.50	−0.30
H$_{10}$	1.35	−5.14	−0.43	H$_{31}$	3.22	−3.27	−0.35
H$_{11}$	−1.35	−5.14	−0.43	C$_{32}$	2.46	2.49	−0.30
C$_{12}$	1.15	2.90	−0.30	H$_{33}$	3.22	3.27	−0.35
C$_{13}$	0.68	4.29	−0.37	C$_{34}$	−2.47	2.50	−0.30
C$_{14}$	−0.69	4.29	−0.37	H$_{35}$	−3.23	3.27	−0.35
C$_{15}$	−1.15	2.90	−0.30	C$_{36}$	−2.47	−2.50	−0.30
H$_{16}$	1.35	5.14	−0.43	H$_{37}$	−3.23	−3.27	−0.35
H$_{17}$	−1.35	5.14	−0.43	C$_{38}$	0.02	0.00	2.54
C$_{18}$	2.95	1.14	−0.31	H$_{39}$	0.54	0.90	2.88
C$_{19}$	4.29	0.71	−0.44	H$_{40}$	0.54	−0.90	2.88
C$_{20}$	4.29	−0.71	−0.44	H$_{41}$	−1.02	0.00	2.90
C$_{21}$	2.95	−1.14	−0.31				

[a] On the atomic numbering, see Figure 5.

a buffer of the excessive electric charge. In fact, we have confirmed that the electric charges for Pb and the porphyrin ring are respectively +1.45 and −2.23 in MePbP⁻, whereas they are +1.00 and −1.00 in PbP. Therefore, Pb−P bond in MePbP⁻ has a much more ionic character than that in PbP, and the Pb−P bond is energetically stabilized.

3.2. Electronic Structure of Sn(II) Porphyrin. Because an experimental result of MePbP⁻ is not available, we cannot verify the calculated results of MePbP⁻. Instead, Guilard et al. synthesized bimetallic metal−metal bonded porphyrins PSnFe-(CO)₄.[7] Because lead and tin atoms are the same group elements,
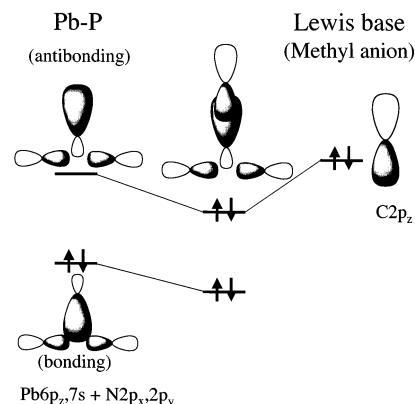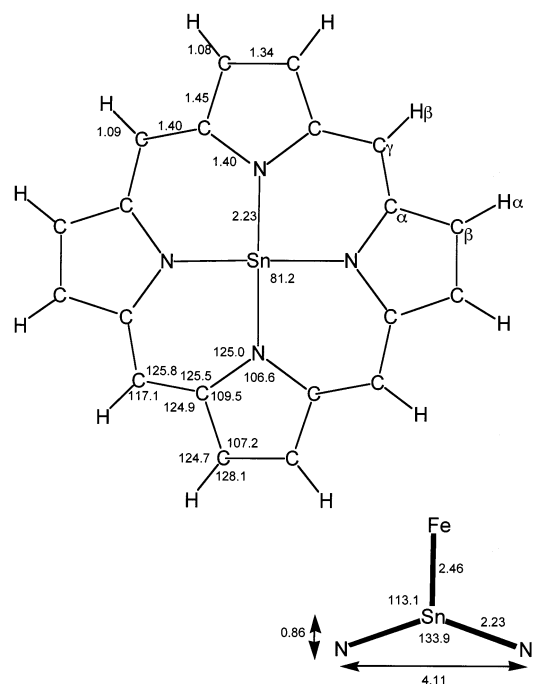
we expect that both Sn porphyrins and Pb porphyrins have similar electronic properties and thus similar metal−ligand bonds are constructed in the Sn(II) porphyrin. Then, we analyze the electronic properties of PSnFe(CO)₄ using a model system in the same way of the case of MePbP⁻. Let us first perform the geometry optimization of SnP. As was expected, the optimum structure of SnP is very similar to that of PbP and reasonably agrees with the geometry determined by the X-ray structure analysis.[26] As well as PbP, SnP has also a nonplanar structure where the center metal is out of the porphyrin plane. To understand the nature of the Sn−Fe bond, we have performed the geometry optimization using a model system (FeSnP) where Fe is located just above Sn. Structural parameters of the optimum geometry of FeSnP are shown in Figure 7 and Table 3. The Sn−Fe bond mainly consists of the $5p_z$ and 6s orbitals of Sn and the $3d_{z^2}$ orbital of Fe. This bond formation is very similar to the case of MePbP⁻, and thus, the analysis described above is straightforwardly applied to the electronic character of the Sn−Fe bond. In fact, we have computationally confirmed that Fe serves as a Lewis base and attacks the unoccupied antibonding Sn−P orbital which corresponds to the counterpart of the Sn−P bonding orbital.

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TABLE 3: Atomic coordinates of FeSnP

atom[a]	x (Å)	y (Å)	z (Å)
Sn	0.00	0.00	0.42
Fe	0.00	0.00	2.88
N	2.05	0.00	−0.46
C_α	2.88	1.11	−0.56
C_β	4.26	0.69	−0.70
C_γ	2.45	2.45	−0.57
H_α	5.11	1.36	−0.80
H_β	3.22	3.22	−0.64

[a] On the Greek alphabet, α, β, and γ, see Figure 7.

4. Concluding Remarks

To investigate the electronic structure of the Pb(II) porphyrin complex (PbP), we have performed ab initio calculations based on a density functional theory. The calculated optimum structure of PbP reasonably agrees with that determined by the X-ray structure analysis. The bond between Pb and the porphyrin ring is mainly constructed from $6p_z$ and $7s$ orbitals of Pb and $2p_x$ and $2p_y$ orbitals of the four nitrogen atoms. Because the counterpart of this bonding orbital is the unoccupied antibonding orbital spreading out opposite to the porphyrin ring, it can be easily attacked by a Lewis base. We have computationally confirmed that a Lewis base, CH_3^-, adds to the center metal of Pb. The similar bond formation has been demonstrated in another group 14 metal (Sn) complex, FeSnP. We expect that various group 14 metalloporphyrin complexes will be synthesized by taking advantage of those bond formations.

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