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Electronic Properties of Palladium−Thiolate Complexes with Tiara-like Structures

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The electronic structures and properties of palladium−thiolate complexes, $Pd_n(SCH_3)_{2n}$ with $n = 6$ and 8, have been investigated by carrying out density functional calculations. The complexes have characteristic tiara-like structures, that is, the palladium atoms form a hexagonal or octagonal ring and each adjacent pair of the palladium atoms is bridged by the sulfur atoms from both sides of the palladium ring. It has been found that Pd−S π bonds play a crucial role in constructing and stabilizing such tiara-like structures. In fact, there exist the Pd−S π bonding orbitals distributing throughout the tiara ring. The Pd−S π bonding interaction also accounts for the reason $Pd_n(SCH_3)_{2n}$ with $n = 6$ and 8 are much more stable than other complexes with different n.

1. Introduction

Metal−thiolate compounds have been investigated intensively in various areas of coordination chemistry,[1−3] cluster and surface science,[4−6] molecular electronics,[7,8] and biotechnology.[9] This is partly because metal−thiolate interaction is unique in a sense that thiolate groups have a strong affinity to a number of metals, and an ability to bridge (or coordinate) two or more metal atoms. These characteristic properties produce a huge number of metal−thiolate complexes with a large variety of structures associated with functions such as optical response, conductivity, catalysis, and magnetism.

In cluster science, it has already been possible to prepare size-selected metal nanoparticles passivated by a monolayer of thiol molecules.[4,10] Then such monolayer protected metal clusters, in general, display different physicochemical properties from corresponding bulk metals. In particular, electronic properties of gold clusters and surfaces passivated by thiolate groups have been studied extensively both experimentally[4−6] and theoretically.[11−19]

In the recently growing area of molecular electronics, a single molecule coupled to noble metal electrode through thiolate groups has been as a promising candidate of molecular wire junctions conducting electrical current.[7,8]

Metal−thiolate compounds have high potentialities for creating a new class of nanoparticle or surface science as mentioned, whereas their experimental and theoretical investigations are still in a juvenile stage. From a viewpoint of theoretical study, to make these metal−thiolate compounds act as functional elements by taking use of their characteristic properties, it is necessary to understand electronic properties of metal−thiolate interaction, and then to reveal fundamental physicochemical properties of the compounds.

In this article, we report electronic structures and properties of palladium thiolates $Pd_n(SCH_3)_{2n}$ with $n = 6$ and 8 with an emphasis on a theoretical description of the metal−thiolate interaction. Kunchur synthesized a palladium *n*-propanethiolate, $Pd_6(SC_3H_7)_{12}$, and found that the complex had a characteristic structure like a tiara.[20] According to his analysis, six palladium atoms formed an almost planar hexagonal ring, and each adjacent pair of the palladium atoms was bridged by the sulfur atoms from both sides of the palladium ring. A similar palladium−thiolate complex with a tiara-like structure, $Pd_8(SC_3H_7)_{16}$, was also synthesized.[21] It is denoted that a number of nickel−thiolates with similar tiara structures have already been synthesized.[22] Although extensive studies on metal−thiolates with characteristic tiara structures have been made experimentally so far, relatively little is known theoretically about electronic structures and properties of those palladium− or nickel−thiolate complexes.[23] Therefore, we carry out herein density functional calculations of the palladium−thiolates and analyze their electronic properties in detail.

This paper is organized as follows. In the next section, we define theoretical models based on real palladium thiolates. The method of calculations is also described in this section. In section 3, we analyze the calculated results. The optimized geometries and their electronic properties are reported. Finally, the concluding remarks are given in section 4.

2. Method of Calculation

We calculate the electronic structures of the palladium−methanethiolate complexes, $Pd_n(SCH_3)_{2n}$ with $n = 6$ and 8, which are in this article referred to as hexamer and octamer, respectively. Although the real complexes in the experiments are palladium−*n*-propanethiolates,[20,21] it is reasonable to assume that the *n*-propyl group has little influence on electronic properties of the main tiara structure. The electronic structures have been calculated at the level of the Kohn−Sham density functional theory (KS-DFT). The calculations employed the Becke three-parameter hybrid exchange functional with the Lee−Yang−Parr correlation functional (B3LYP).[24] A 28-electron relativistic effective core potential was utilized for the palladium atom and the remaining 18 valence electrons were explicitly treated. The standard double ζ basis set (LanL2DZ) was employed for all elements.[25,26] All the calculations have been performed within the GAUSSIAN 98 package of programs.[27]

3. Results and Discussion

3.1. Optimized Geometries of the Palladium−Thiolate Hexamer and Octamer. The optimized geometry of the

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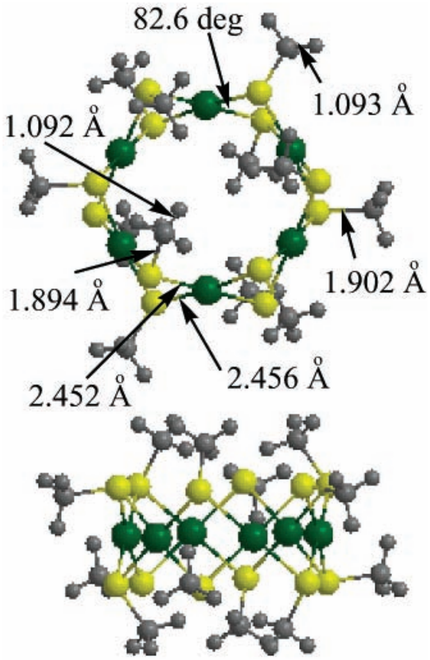

Figure 1. Optimized geometry of the palladium−thiolate hexamer $Pd_6(SCH_3)_{12}$ in top and side views: Pd(green), S(yellow), CH_3(gray).

TABLE 1: Structural Parameters of the PdS_4 Units for the Palladium−Thiolate Hexamer and Octamer in Comparison with the Results of X-ray Structural Analyses

	hexamer		octamer	
parameter	cal	exp[a]	cal	exp[b]
Pd−S bond (Å)	2.46	2.33	2.45	2.32
dihedral angle (deg)	176.6	176.4	177.5	177.3

[a] Reference 20. [b] Reference 21.

palladium−thiolate hexamer is shown in Figure 1. The figure illustrates a characteristic tiara structure of the hexamer; i.e., six palladium atoms (green) form an almost planar hexagonal ring, and the sulfur atoms (yellow) bridge each adjacent pair of the palladium atoms from both sides of the palladium ring. The methyl groups (gray) are disposed alternately axial or equatorial. This alternation would arise from a steric effect. Figure 1 also shows that the hexamer consists of six facets of an approximately rectangular plane in which the palladium atom is surrounded by the four sulfur atoms at the corners. Each two of these PdS_4 units shares the two sulfur atoms. This is rather reasonable because divalent palladium complexes are generally known to form a square planar structure with four-coordination preferably. The PdS_4 unit is, in reality, distorted from an ideal plane to a square pyramidal structure, in which the palladium atom is displaced out of the plane. The degree of its planarity is easily evaluated by a dihedral angle of the PdS_4 unit. Structural parameters of the dihedral angle and the Pd−S bond distance of the unit are listed in Table 1 in comparison with those determined by the X-ray structural analysis.[20] Because the full geometry optimization has been carried out with no constraint of molecular symmetry, the calculated structural parameters are mean values as well as experimental ones. Both structural parameters reasonably agree with experimental results, and the PdS_4 unit was found to be an almost planar structure.

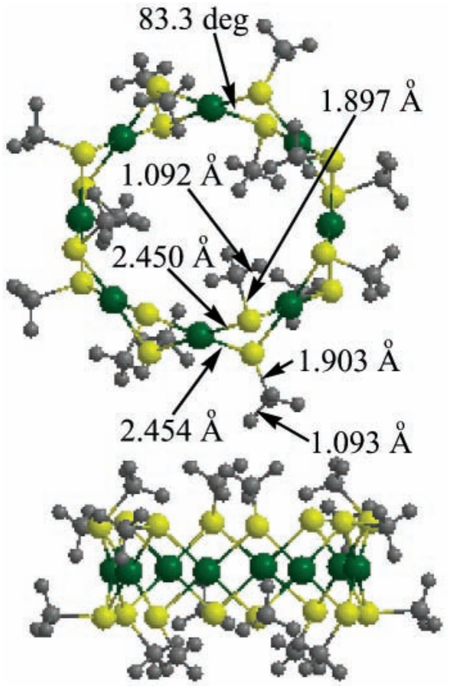

Figure 2. Same as Figure 1 but for the palladium−thiolate octamer, $Pd_8(SCH_3)_{16}$.

The optimized geometry of the palladium−thiolate octamer is shown in Figure 2. As is clearly seen from the figure, the octamer is very similar to the hexamer except that the palladium atoms form an octagonal ring. In Table 1, we list the structural parameters of the PdS_4 unit for the octamer. Both structural parameters reasonably agree with those determined by the X-ray structural analysis,[21] and the PdS_4 units for the hexamer and the octamer have almost the same structure.

Before elucidating the electronic properties of the complexes, we should refer to the molecular symmetry of the hexamer and the octamer. We have determined the structures of the complexes by performing full geometry optimization without assuming molecular symmetry. However, the optimized geometries of the hexamer and the octamer were found to be nearly D_{3d} and D_{4d} molecular symmetries, respectively. Thus, we performed constrained geometry optimization for the hexamer (D_{3d}) and the octamer (D_{4d}) and found that the total energies of the constrained complexes were slightly higher (∼100 meV) than the unconstrained complexes. We furthermore confirmed that the structural parameters of the constrained (D_{3d} and D_{4d}) complexes remained almost unchanged from those of the unconstrained (C1) complexes; all the atom−atom distances are unchanged within 0.005 Å. Therefore, for the sake of simple and clear discussion in the remainder of this article, we analyze the electronic properties of the hexamer and the octamer with D_{3d} and D_{4d} molecular symmetries, respectively, unless otherwise stated. It should be noted that the following discussion qualitatively (and almost quantitatively) holds true in both cases of the complexes with and without (i.e., full optimization) the molecular symmetry.

3.2. Kohn−Sham Orbital Analyses. Figure 3 shows Kohn−Sham (KS) orbital energy diagrams for the hexamer and the octamer. The energies are indicated in electronvolts relative to the energy of the highest occupied molecular orbital (HOMO). Both of the energy diagrams have similar band structures and are allowed to be classified into four groups: (i) C 2s and S 3s orbitals, (ii) C−H bonding orbitals, (iii) C−S bonding orbitals, and (iv) Pd 4d and S 3p lone pair orbitals, and Pd−S bonding orbitals. As is clearly seen from the figure, groups i and ii are well separated. Although the boundary between groups iii and iv is somewhat ambiguous, we have computationally confirmed that almost all of the C−S bonding orbitals locate in the energy range of group iii.

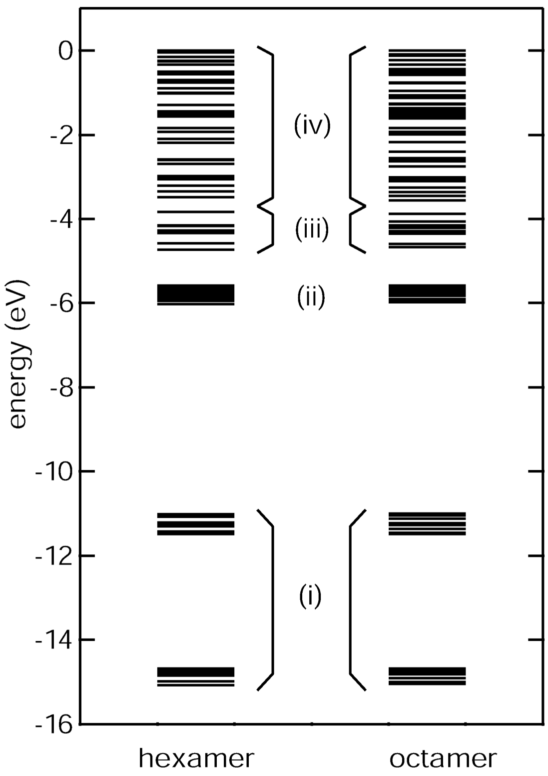

Figure 3. Kohn−Sham orbital energies of the palladium−thiolate hexamer and octamer. The energies are indicated in electronvolts relative to the HOMO energy. For details of the orbital categorization (i)−(iv), see text.

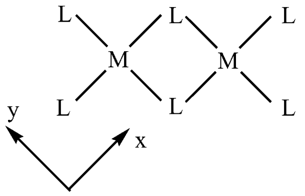

Figure 4. Schematic diagram of a bridged complex of d^8 metal ions. The uppercase alphabetic characters M and L represent a certain d^8 metal ion and ligand, respectively.

The electronic properties of the tiara structure are reasonably explained in terms of a square coordination character of Pd(II) complexes. There are two types of the Pd−S interaction contributing to formation of the tiara structure, i.e., Pd−S σ and π bonds. It is well-known that d^8 metal ion such as Pd(II) and Pt(II) favorably forms square planar complexes with four-coordination because $d_{x^2-y^2}$ orbital constructs sp^2d hybrid orbital together with s, p_x, and p_y orbitals.[28] The hybrid orbital points toward four corners of a square plane and then forms four metal−ligand σ bonds. Furthermore, such square planer complexes tend to form polynuclear complexes bridged by halogens, tertiary phosphines, and thiolates.[28] Consequently, bridged complexes of d^8 metal ions are schematically illustrated in Figure 4. On the other hand, the four metal d_{xy}, d_{xz}, d_{yz}, and d_{z^2} orbitals remain almost pure atomic d orbitals, and the ligand p_z orbital does not contribute to the metal−ligand σ bonds. However, it is possible to form metal−ligand π bonds through the interaction between the metal d_{xz} (or d_{yz}) and ligand p_z orbitals. In the palladium−thiolate complexes, these characteristic metal−ligand interactions such as (i) Pd(sp^2d)−S(p_x,p_y) σ bond, (ii) bridged structure via the methanethiolate, and (iii) Pd(d_{xz},d_{yz})−S(p_z) π bond are realized. If the bridged structure is completed in a circle, the tiara structure is formed. (It is apparent that each plane of the PdS_4 units of the tiara complexes faces in different direction. We here refer to the *xy*-plane as the plane of the PdS_4 unit for convenience in discussion.) We should remark that the sulfur atoms with the equatorial methyl group do not form the Pd−S π bond because the S 3p orbital perpendicular to each PdS_4 facet forms the S−C σ bond. Because the hexamer and the octamer have the axial and equatorial methyl groups alternatively, half of the sulfur atoms (i.e., the sulfur atoms with the axial methyl group) form the Pd−S π bond in a zigzag along the tiara ring. In fact, we found characteristic Pd−S π bonding orbitals distributing throughout the tiara ring. Figure 5, for example, illustrates the lowest Pd−S π bonding orbital of the hexamer. The red and blue colors indicate opposite phases of the orbital.

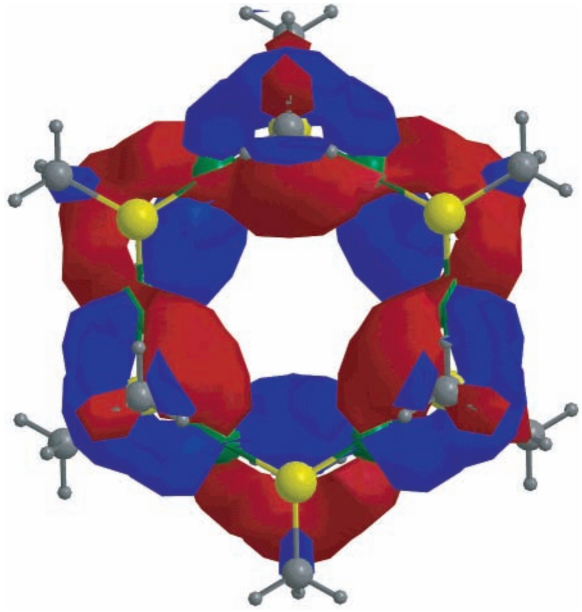

Figure 5. Lowest Pd−S π bonding orbital in the palladium−thiolate hexamer.

We further make a comment on the bonding character of Pd−S with the equatorial methyl group. As mentioned above, the sulfur atoms with the equatorial methyl group do not form the Pd−S π bond out of the PdS_4 plane. However, these sulfur p_x (or p_y) orbitals interact with the Pd d_{xy} orbitals in the PdS_4 plane. This interaction somewhat corresponds to the Pd−S π bond in the plane although it is not a clear π bond, unlike the Pd−S(axial) π bond, because the S(equatorial) p_x (or p_y) orbitals also contribute to the Pd−S σ bond in the plane. As a result, the Pd−S(equatorial) bond has a bond length similar to the Pd−S(axial) one. In fact, the Pd−S(equatorial) bond length is slightly longer (~0.004 Å) than the Pd−S(axial) bond length (see Figures 1 and 2). This small value is attributed to difference in character of the Pd−S π bonds in the Pd−S plane and out-of-plane.

3.3. Pd−S π Bond Relevant to the Tiara Structure. We have restricted ourselves to the palladium−thiolate hexamer and octamer because both complexes were synthesized favorably.[20,21] This fact means that other oligomers should have something disadvantageous to the hexamer and the octamer. In the present subsection, let us first explain the reason for the disadvantage of odd-membered oligomers to even-membered ones, and then reveal the origin of the energetically favorable structures of the hexamer and the octamer.

3.3.1. Even- and Odd-Membered Palladium−Thiolates. As was described above, the Pd−S π bonds in each PdS_4 unit are connected in a zigzag and then the totally closed π bonding orbital is formed throughout the hexagonal or octagonal ring.

TABLE 2: Structural Parameters of the PdS_4 Units for the Palladium−Thiolate Tetramer, Hexamer, and Octamer[a]

parameter	tetramer	hexamer	octamer
Pd−Pd distance (Å)	3.04	3.27	3.40
dihedral angle (deg)	160.9	176.6	177.5

[a] Pd−Pd distance is the metal−metal distance between adjacent units. A dihedral angle indicates a degree of planarity of the units.

It is easy to understand that such a closed π bonding orbital cannot be completed in the case of odd-membered oligomers because their orbitals as a whole are out of phase. We have performed geometry optimization for the palladium−thiolate pentamer with a tiara-like structure as an example of odd-membered oligomers. The calculation failed to converge at the present level of theory, and we could not find a stable structure of the pentamer. If the formation of the totally closed π bonding orbital significantly contributes to stabilization of the tiara complexes, we can account for the fact that even-membered palladium−thiolates exist more favorably than odd-membered ones. To verify this conjecture, we evaluate energies of stabilization when forming the totally closed π bonding orbital.

Because the following discussion can be qualitatively applied to the case of the palladium−thiolate octamer, we analyze the π bond formation for the hexamer. The complex has three π bonding orbitals distributing throughout the palladium ring. These three orbitals are classified into two types in terms of irreducible representations of D_{3d} symmetry. One is the lowest orbital with a_{2u} representation and the other is a doubly degenerate orbital with e_g one. Furthermore, we have found three π antibonding orbitals that are classified into higher a_{1u} and lower doubly degenerate e_u orbitals. The π antibonding orbitals are the counterparts of three π bonding orbitals. The relative energies of the Pd−S π bonding and antibonding orbitals are −2.930 eV (a_{2u}), −2.737 eV (e_g), +5.649 eV (e_u), and +9.898 eV (a_{1u}). These energy levels clearly show that the π bond formation significantly stabilizes the palladium−thiolate hexamer.

3.3.2. Energetically Favorable Structures of the Hexamer and the Octamer. We now theoretically verify whether other even-membered palladium thiolates exist except for the hexamer and the octamer. To this end, we have performed full geometry optimization of the palladium−thiolate tetramer with a tiara structure as an example. Let us first compare stabilization energies of three types of the palladium−thiolate complexes, tetramer, hexamer, and octamer. All of the palladium−thiolate complexes formally include a common minimum unit of $Pd(SCH_3)_2$; i.e., the tetramer have four minimum units, the hexamer six, and the octamer eight. Then, we simply calculate the unit energy $\tilde{E}_n$ of $Pd(SCH_3)_2$ defined by $\tilde{E}_n = E_n/n$, where E_n are the total energies of the complexes with $n = 4$ (tetramer), 6 (hexamer), and 8 (octamer) being the numbers of the $Pd(SCH_3)_2$ minimum unit. (To quantitatively obtain the stabilization energy, $\tilde{E}_n$ are calculated for the fully optimized geometries with no constrain of molecular symmetry.) The stabilization energies relative to $\tilde{E}_4$ are $\tilde{E}_6 - \tilde{E}_4 = -0.501$ eV and $\tilde{E}_8 - \tilde{E}_4 = -0.519$ eV. These results clearly indicate that the tetramer is less stabilized than the hexamer and the octamer. The disadvantage of the tetramer is caused by its structural character. In Table 2, we list metal−metal distances between adjacent PdS_4 units and dihedral angles in the unit for the fully optimized complexes. The dihedral angle represents the degree of planarity of the PdS_4 unit. The structural parameters of the tetramer are apparently different from those of the hexamer and the octamer. Because the size of the tetragonal ring is smaller than those of the hexamer and the octamer, the Pd−Pd distance becomes closer. Owing to the repulsive Pd−Pd interaction, the PdS_4 unit of the tetramer is distorted largely from a complete plane. Consequently, the Pd−S π bonding orbital is also distorted and it leads to destabilization of the tetragonal tiara complex, and thus the hexamer and the octamer favorably exist.

4. Concluding Remarks

Density functional calculations have been performed to investigate electronic structures and properties of palladium−thiolate complexes $Pd_n(SCH_3)_{2n}$ with n=6 and 8. It has been found that the complexes have characteristic tiara-like structures. According to the present calculations, six or eight palladium atoms form an almost planer hexagonal or octagonal ring, and the sulfur atoms bridge each adjacent pair of the palladium atoms from both sides of the palladium ring. These optimized geometries reasonably agree with those obtained by the X-ray structural analyses. Detailed analyses of the KS orbitals of the complexes have revealed that the formation of the tiara structure is attributed to three important Pd−S bonds originating from a square coordination character of Pd(II) complexes: (i) the Pd-(sp^2d)−S σ bond, (ii) the bridged structure via the methanethiolate, and (iii) the Pd−S π bond. In particular, the Pd−S π bonding orbitals distributing throughout the palladium ring play a crucial role in constructing and stabilizing the tiara structures. The stabilization is found to be much more efficient in even-membered complexes than in odd-membered ones. Although the palladium−thiolate hexamer and octamer were favorably synthesized, we computationally confirmed the presence of the tetramer. However, it was found that the tetramer was less advantageous to form tiara-like structure than the hexamer and the octamer. This is due to the fact that the adjacent metal−metal distance becomes shorter and thus the PdS_4 unit is distorted largely. The distortion significantly affects on the Pd−S π bonding such that the tetra-tiara ring becomes destabilized.

Before ending this article, we briefly comment on nickel−thiolates with a tiara structure. Although nickel−thiolates with a hexagonal tiara structure have been synthesized favorably, odd-membered tiara complexes were also structurally characterized.[22] Furthermore, some of those complexes have a more unique structure of an irregular convex/concave-shaped cyclic ring, in other words, a distorted tiara ring.[22] Our preliminary calculations have demonstrated that nickel−thiolate hexamer and octamer are stable owing to the same reason described in this article. It is interesting to reveal a new mechanism that stabilizes such odd-membered nickel−thiolates.

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