

## Geometrical Characteristics and Atomic Charge Variations of Pd(II) Complexes [Pd(L)Cl<sub>2</sub>] with an Axial (Pd···O) Interaction

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Geometrical structures of [Pd(L)Cl<sub>2</sub>] with oxathia macrocycles have been calculated using *ab initio* second-order Möller-Plesset (MP2) and Density Functional Theory (DFT) methods with triple zeta plus polarization (TZP) basis set level. In optimized Pd(L)Cl<sub>2</sub> complexes, Pd(II) locates at the center surrounded by a square planar array of two sulfurs on an oxathia macrocycle and two chlorides. The *endo*-Pd(II) complexes with an axial (Pd···O) interaction are more stable than the *exo*-Pd(II) complexes without the interaction. In the *endo*-Pd(II) complexes, the atomic charge of the oxygen atom moves to Pd(II) via the axial (Pd···O) interaction and then, the charge transfer from Pd(II) to the S-atoms occurs stepwise via  $\pi$ -acceptors of the empty d-orbitals.

**Key Words :** Atomic charge, Oxathia macrocycle, Density functional theory, Pd(II) complex, Axial (Pd-O) interaction

### Introduction

Using homoletic and heteroletic macrocyclic ligands containing electronegative atoms, the unusual geometrical structures, oxidation states, and ion-selective characteristics of transition metal(II) macrocyclic complexes [M(L)Cl<sub>2</sub>] have been extensively investigated by the experimental and theoretical researches.<sup>1-21</sup> The bindings between the transition metals and macrocyclic ligands are formed by the coordination of the N- and O-atoms (hard  $\sigma$ -donor property) and the S-atom (soft  $\sigma$ -donor and  $\pi$ -acceptor properties) on the ligand. In the experimental results of Schröder's group,<sup>1-7</sup> the crystal structures of the Pd(II) complexes have a square-planar Pd(II) center bound to the N-, O-, and S-atom donors. In *endo*-Pd(II) complexes, an apically long-range (Pd···L) interaction of ( $R_{\text{Pd}\cdots\text{L}}$ ) = 2.952~3.033 Å between Pd(II) and the apical L-atom is formed.<sup>1-3</sup> The geometrical structures of the metal-macrocycle complexes are a distorted octahedral geometry about the centrosymmetric Pd(II) complexes with the four equatorial thia donors and the two apically coordinated donors. The distances of the apical (Pd···L) interaction are longer than the values of a Pd-S (Pd-N and Pd-O) bond observed normally. In the complex oxidation from M(II) to M(III), the structural changes [elongation of (Pd···S)] of the thioether macrocyclic complexes are occurred from the  $\pi$ -acceptor property using empty d-orbitals on the S-atom.<sup>2</sup> In the complex oxidation, the metal complexes are electronically controlled by the metal-donor atom interactions rather than by any conformational and configurational constraints of the macrocyclic ligands.<sup>4</sup> Meanwhile, in *cis*-dichloro Pd(II) complexes,<sup>5-7</sup> the Pd-S distances of the two equatorial thia donors are shorter than

those of Pd(II) complexes coordinated with four equatorial thia donors. The decrease of the Pd-S distances have been suggested that  $\pi$ -back donation from the Pd(II) ion to the S atoms may be occurring with  $\pi$ -donation from X<sup>-</sup> (Cl<sup>-</sup>, Br<sup>-</sup>) to Pd(II).

The structural characterizations of the Pd(II) complexes are analyzed using crystallographic and NMR spectroscopic experiments.<sup>8-10</sup> By the additional donor sites within the macrocyclic ligands, the square planar structure of the Pd complexes gives a kind of five coordinate complex. The distance (2.92 Å) of the axial (Pd···S) interaction between Pd(II) and the apical sulfur atom is in excess of the normal bonding range for Pd-S distance (2.30-2.50 Å). The longer distance is evidence for a  $\sigma$ -donor (O-atom) - cation [M(II)] interaction. As a result, the structures of the Pd(II) complexes have a five-coordinate, distorted square pyramidal geometry. While, without the presence of an axial (Pd···L) interaction, the macrocyclic ligands in [Pd(L)Cl<sub>2</sub>] of the solid state are coordinated in a fashion similar to a square pyramidal geometry. The central Pd(II) atom is not co-planar with the donor set. Two of the donor atom set lies above the mean plane and two atoms below.

Although the unusual coordination structures, relative stabilities, and oxidation states of the complexes have already been studied by many groups, further investigations seem to be worth carrying out on the base of following points. i) According to *exo*- or *endo*-type in the same complex, the relative stabilities are different from each other. Which conformers are more stable isomer? ii) In Pd(II) macrocyclic complexes, Pd(II) locates at the center surrounded by two sulfurs on bidentate macrocyclic ligand and two chlorides. How are the geometrical structures of the Pd(II) complexes coordinated to the central Pd(II) cation? iii) The axial (Pd···O) interactions in *endo*-Pd([9]aneS<sub>2</sub>O)Cl<sub>2</sub> and *endo*-Pd(*o*-S<sub>2</sub>O)-Cl<sub>2</sub> exist. Are the atomic charges in the complexes varied by

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the (Pd...O) interaction? iv) In the Pd(II) complexes, is the binding energy as low as 2-5 kcal/mol?

### Computational Methods

The equilibrium geometrical structures of 1-oxa-4,7-dithiacyclononane ([9]aneS<sub>2</sub>O), 6-oxa-3,9-dithiabicyclo[9.4.0]pentadeca-1(11),12,14-triene (*o*-S<sub>2</sub>O), Pd([9]aneS<sub>2</sub>O)Cl<sub>2</sub>, and Pd(*o*-S<sub>2</sub>O)Cl<sub>2</sub> were optimized with the second-order Møller-Plesset (MP2) level using the Gaussian 98.<sup>22</sup> To confirm the existence of the stable structures, the harmonic vibrational frequencies of the species have been analyzed at the Hartree-Fock (H-F) level.

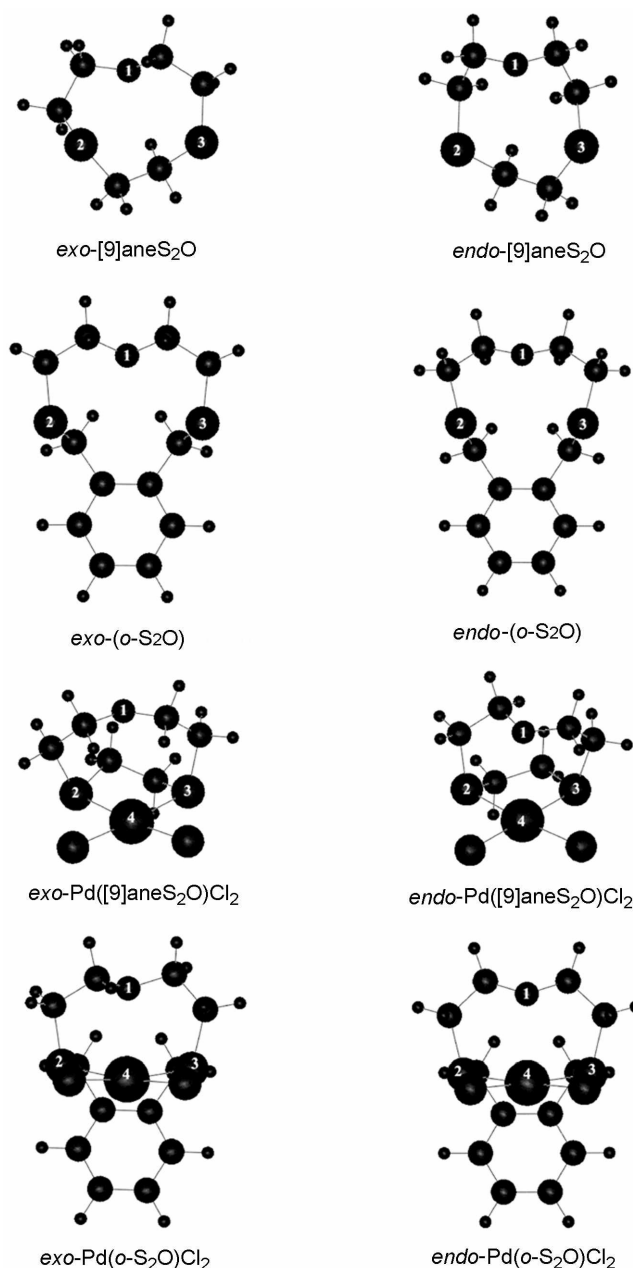
The geometrical structures of the macrocyclic ligands and Pd(II) complexes were optimized with the density functional scheme<sup>23</sup> using the Gaussian 98 packages. The following Gaussian-type basis sets were used; (63321/531/41) for transition Pd metal with the uncontracted auxiliary basis sets of (10/5/5), (6321/521/1) for Cl with the uncontracted auxiliary basis sets of (9/4/4). The geometrical optimizations were self-consistently performed within the local spin density (LSD) approximation. After that, nonlocal corrections proposed by Becke<sup>24</sup> and Perdew<sup>25</sup> for the exchange and correlation interactions have been applied, which can improve the energies of LSD approximation to the similar level as the MP2 method.

The basis sets chosen were the double zeta basis on Pd (3s3p4d/3s2p2d),<sup>26</sup> The triple-zeta GTO basis sets<sup>26</sup> for chloride (3s, 3p) were augmented with single 4d polarization function for Cl. Effective Core Potential (ECP)<sup>22</sup> including relativistic contributions are used to represent 28 innermost (up to 3d) electrons of the Pd atom (lanl2dz) and standard 6-31+G\* basis sets are used for other atoms except donor atom as C, O, and S where 6-31+G\*\* basis sets are used.

### Results and Discussion

Geometrical structures of 1-oxa-4,7-dithiacyclononane ([9]aneS<sub>2</sub>O), 6-oxa-3,9-dithiabicyclo[9.4.0]pentadeca-1(11),12,14-triene (*o*-S<sub>2</sub>O), Pd([9]aneS<sub>2</sub>O)Cl<sub>2</sub>, and Pd(*o*-S<sub>2</sub>O)Cl<sub>2</sub> are optimized at the DFT level and the most stable isomers of the *exo*- and *endo*-types are represented in Figure 1. The geometrical structures of *o*-S<sub>2</sub>O and *endo*-Pd(*o*-S<sub>2</sub>O)Cl<sub>2</sub> have C<sub>s</sub>-symmetry, while, the structures of the other ligands and Pd-complexes have C<sub>1</sub>-symmetry. According to arrangement of the oxygen and sulfur atoms on the oxathia macrocyclic ligand, the structures of the ligands are divided as two groups by *exo*- and *endo*-oriented conformers. In *exo*-oriented conformer, an oxygen atom on the ligands is directing towards the opposite direction against two sulfur atoms, while, in *endo*-oriented conformer, the oxygen atom is directing towards the same direction. The geometrical structure of [9]aneS<sub>2</sub>O is formed by a 9-membered cyclic chain consisting of three ethylene units, two sulfur atoms, and an oxygen atom. The structure of *exo*-[9]aneS<sub>2</sub>O can be a bidentate macrocyclic ligand by two sulfur atoms. Meanwhile, the structure of *endo*-[9]aneS<sub>2</sub>O can be a kind of

tridentate macrocyclic ligand. That is, the two sulfur atoms having both soft  $\sigma$ -donor and  $\pi$ -acceptor properties can be coordinated to the central Pd(II) cation at the square planar geometry and one oxygen atom as a hard  $\sigma$ -donor property can be simultaneously coordinated to Pd(II) via an apically long-range interaction. To reduce the flexibility and the steric hindrance of the macrocyclic frame, *o*-S<sub>2</sub>O as a macrocyclic ligand is chosen. The geometrical structure of *o*-S<sub>2</sub>O is a bridged structure in which the macrocyclic frame of [9]aneS<sub>2</sub>O is bonded by a cyclophane group. The structure of *o*-S<sub>2</sub>O is more rigid and symmetric than that of [9]aneS<sub>2</sub>O. Oxathia macrocyclic ligands can serve as  $\sigma$ -



**Figure 1.** Optimized geometrical structures of 1-oxa-4,7-dithiacyclononane ([9]aneS<sub>2</sub>O), 6-oxa-3,9-dithiabicyclo[9.4.0]pentadeca-1(11),12,14-triene (*o*-S<sub>2</sub>O), and palladium(II) transition metal complexes (Pd([9]aneS<sub>2</sub>O)Cl<sub>2</sub> and Pd(*o*-S<sub>2</sub>O)Cl<sub>2</sub>) at the DFT/6-31+G\*\* level. 1, 2(3), and 4 denote O, S, and Pd(II), respectively.

donors *via* donation of the available lone pair electrons and as  $\pi$ -acceptors using empty d-orbitals of the sulfur atom.

In optimized Pd(L)Cl<sub>2</sub> complexes, the geometrical structures are more symmetric and compacted than those of the corresponding macrocyclic ligands. Pd(II) locates at the center surrounded by square planar geometry of two sulfurs and two chlorides. The macrocyclic ligands are located at the side plane of the square planar geometry. When the *exo*- or *endo*-macrocyclic ligand (L) coordinates to Pd(II), the geometrical conformers of the [Pd(L)Cl<sub>2</sub>] complexes can be existed two corresponding conformations of *exo*- or *endo*-type. In the *exo*-Pd(II) complexes, an oxygen atom on the macrocycle is directing towards the outer side of the central

Pd(II) metal. While, the oxygen atom in the *endo*-Pd(II) complexes is directing toward the inner side.

In *endo*-Pd([9]aneS<sub>2</sub>O)Cl<sub>2</sub> and *endo*-Pd(*o*-S<sub>2</sub>O)Cl<sub>2</sub>, the axial (Pd...O) interaction between the central Pd(II) cation and an oxygen atom on the macrocyclic ligands is formed. The oxygen atom of the *endo*-Pd(L)Cl<sub>2</sub> complex plays a role of the third electron donor group to the central Pd(II) metal. As a result, the structures of Pd([9]aneS<sub>2</sub>O)Cl<sub>2</sub> and Pd(*o*-S<sub>2</sub>O)Cl<sub>2</sub> show that the more stable conformer is *endo*-dentate fashion. The oxygen atom in the *endo*-dentate complexes lies above the *endo*-Pd(L)Cl<sub>2</sub> coordination plane by the (Pd...O) distance of 2.944–2.974 Å. According to a long range (Pd...O) interaction, the structures of *endo*-type

**Table 1.** Relative potential energies (eV) between two conformers, optimized geometrical parameters (Å), and atomic charges (au) of stable *exo*- and *endo*-conformers of the Pd(II) complexes and the oxathia macrocyclic ligands obtained at the MP2 and DFT methods

	R.E. <sup>a</sup>	R <sub>Pd-Cl</sub> <sup>b</sup>	R <sub>Pd-S</sub> <sup>c</sup>	R <sub>Pd-O</sub> <sup>d</sup>	R <sub>S1-S2</sub> <sup>e</sup>	R <sub>S-O</sub> <sup>f</sup>	Pd <sup>g</sup>	S <sub>1</sub> <sup>h</sup>	S <sub>2</sub> <sup>h</sup>	O <sup>i</sup>	Cl <sup>j</sup>
<i>exo</i> -[9]aneS <sub>2</sub> O											
MP2	0.0				3.544	3.230		0.102	0.104	-0.682	
DFT	0.0				3.625	3.284		0.031	0.041	-0.676	
<i>endo</i> -[9]aneS <sub>2</sub> O											
MP2	0.19				3.538	3.145		0.150	0.154	-0.669	
DFT	0.15				3.602	3.115		0.070	0.082	-0.661	
<i>exo</i> -( <i>o</i> -S <sub>2</sub> O)											
MP2	0.0				3.987	3.098		0.136	0.136	-0.670	
DFT	0.0				4.013	3.191		0.021	0.021	-0.678	
<i>endo</i> -( <i>o</i> -S <sub>2</sub> O)											
MP2	0.17				3.878	2.992		0.162	0.162	-0.659	
DFT	0.14				3.961	3.086		0.024	0.024	-0.653	
<i>exo</i> -Pd([9]aneS <sub>2</sub> O)Cl <sub>2</sub>											
MP2	0.29	2.350	2.382	3.388	3.367	3.189	1.370	-0.554	-0.568	-0.656	-0.377
DFT	0.20	2.349	2.375	3.383	3.361	3.185	1.366	-0.593	-0.597	-0.684	-0.381
exptl <sup>k</sup>		2.313		3.379							
<i>endo</i> -Pd([9]aneS <sub>2</sub> O)Cl <sub>2</sub>											
MP2	0.0	2.348	2.381	2.982	3.358	3.194	1.246	-0.614	-0.616	-0.549	-0.390
DFT	0.0	2.347	2.367	2.974	3.358	3.191	1.238	-0.643	-0.645	-0.558	-0.394
exptl <sup>l</sup>		2.332	2.268	2.968							
exptl <sup>m</sup>			2.332	2.952							
<i>exo</i> -Pd( <i>o</i> -S <sub>2</sub> O)Cl <sub>2</sub>											
MP2	0.25	2.344	2.368	3.377	3.824	3.057	1.391	-0.545	-0.549	-0.657	-0.395
DFT	0.22	2.342	2.346	3.367	3.824	3.055	1.374	-0.581	-0.586	-0.694	-0.402
exptl <sup>n</sup>			2.331								
exptl <sup>o</sup>			2.311								
exptl <sup>p</sup>		2.316	2.311	3.64							
<i>endo</i> -Pd( <i>o</i> -S <sub>2</sub> O)Cl <sub>2</sub>											
MP2	0.0	2.342	2.360	2.958	3.810	4.141	1.254	-0.619	-0.619	-0.531	-0.402
DFT	0.0	2.340	2.342	2.944	3.810	3.138	1.243	-0.658	-0.658	-0.535	-0.419
exptl <sup>q</sup>		2.330	2.317								

<sup>a</sup>Relative potential energies between *exo*- and *endo*-conformers. <sup>b</sup>Average distances between Pd(II) and the chloride atom in [Pd(L)Cl<sub>2</sub>]. <sup>c</sup>Average distances between Pd(II) and the sulfur atom. <sup>d</sup>Distances between Pd(II) and the oxygen atom. <sup>e</sup>Distances between two sulfur atoms. <sup>f</sup>Average distances between the sulfur and oxygen atoms. <sup>g</sup>Atomic charges of Pd(II). <sup>h</sup>Average atomic charges of the sulfur atom. <sup>i</sup>Atomic charges of the oxygen atom. <sup>j</sup>Average atomic charges of the chloride atom. <sup>k</sup>Ref. 17. <sup>l</sup>Ref. 12. <sup>m</sup>Ref. 1. <sup>n</sup>Ref. 6. <sup>o</sup>Ref. 5. <sup>p</sup>Ref. 15 and 16. <sup>q</sup>Ref. 13.

complexes are more symmetric than those of *exo*-type complexes. In *exo*-Pd([9]aneS<sub>2</sub>O)Cl<sub>2</sub> and *exo*-Pd(*o*-S<sub>2</sub>O)Cl<sub>2</sub> complexes, the bidentate macrocyclic ligands complexed by Pd(II) also locate at the axial plane and an oxygen atom is situated along the outer side to the central Pd(II) cation. Pd(II) also locates at the center surrounded by a square planar array of two sulfur and two chlorides. The oxygen atom of the *exo*-dentate conformer also lies above the *exo*-Pd(L)Cl<sub>2</sub> coordination plane by R<sub>Pd...O</sub> of 3.367–3.383 Å. This distance is longer than the sum of the van der Waals radii of the atoms concerned. Our optimized structures of Pd(L)Cl<sub>2</sub> are similar to the various experimental result.<sup>1–20</sup>

By the crystallographic results, various structural characterizations of the Pd(II) complexes are analyzed by McAuley group.<sup>8–10</sup> In *endo*-Pd(L)Cl<sub>2</sub> with an axial (Pd...S) interaction, the distances of the axial interaction are in excess of the normal bonding range of the R<sub>Pd...S</sub> distance (2.30–2.50 Å). Although the axial (Pd...S) interaction is formed in the Pd(II) complexes, the square planar structures of the Pd(II) complexes are distorted in the solid state. The distortion of the Pd(II) coordination geometry indicates a stacking of the cations within the crystalline lattice. Meanwhile, in *exo*-Pd(L)Cl<sub>2</sub> without the interaction, the macrocyclic ligands of the [Pd(L)Cl<sub>2</sub>] complexes are coordinated to be an unusual square pyramidal geometry. The Pd(II) atom is not co-planar with the donor set but lies above the plane at a perpendicular distance of 0.11 Å. And two of the donor atom set lies above the mean plane and the other two atoms below. The observed results are a measure of the lability of the Pd(II) ion and the flexibility of the pendant-arm macrocyclic ligands.

Relative potential energies, geometrical parameters, and atomic charges of optimized macrocyclic ligands and optimized [Pd(L)Cl<sub>2</sub>] complexes are listed in Table 1. The more stable conformers in the oxathia macrocyclic ligands are obtained when the oxygen atom is oriented in *exo*-dentate fashion. In each ligand, the *exo*-conformers are somewhat more stable than *endo*-conformers and they are consistent with experimental results in the other systems.<sup>15,16</sup> Meanwhile, in Pd(II) complexes with an axial (Pd...O) interaction between Pd(II) and the oxygen atom, the geometrical structures of the *endo*-Pd([9]aneS<sub>2</sub>O)Cl<sub>2</sub> and *endo*-Pd(*o*-S<sub>2</sub>O)Cl<sub>2</sub> are more stable (≈ 0.22 eV) than those of the corresponding *exo*-types, respectively. The energy gap between *endo*- and *exo*-Pd(*o*-S<sub>2</sub>O)Cl<sub>2</sub> is larger than that of between *endo*- and *exo*-Pd([9]aneS<sub>2</sub>O)Cl<sub>2</sub>. Our energy difference between *endo*- and *exo*-Pd(L)Cl<sub>2</sub> calculated with the DFT method is about 5 kcal/mol. The small energy difference between *exo*- and *endo* coordination modes of [9]aneS<sub>2</sub>O is investigated by the experimental result.<sup>17</sup> The small energy changes in solvent incorporation or crystal packing forces are factors which may switch *endo*-dentate and *exo*-dentate coordinations of the Pd(II) metal cation with the ligands. This energy gap could be a consequence of enhanced  $\pi$ -back bonding between the sulfur atoms and the Pd(II) center due to increased  $\sigma$ -donation by the apical oxygen atom. This  $\pi$ -back bonding of the Pd-S bond in the dichloride complex could be responsible for the apical *endo*-

dentate structure of Pd([9]aneS<sub>2</sub>O)Cl<sub>2</sub>.

Our distance parameters are compared with the experimental values.<sup>1,5,6,12,13,15–17</sup> The average distances between Pd(II) and sulfur atoms and between sulfur and oxygen atoms are denoted as R<sub>Pd,S</sub> and R<sub>S,O</sub>, respectively. In [9]aneS<sub>2</sub>O and *o*-S<sub>2</sub>O, the distance parameters of *exo*-type calculated with the DFT level are longer than the corresponding parameters of *endo*-type. R<sub>S1,S2</sub> of ≈ 3.63 Å and R<sub>S,O</sub> of ≈ 3.28 Å in *exo*-[9]aneS<sub>2</sub>O are longer than R<sub>S1,S2</sub> of ≈ 3.60 Å and R<sub>S,O</sub> of ≈ 3.12 Å in *endo*-[9]aneS<sub>2</sub>O, respectively. According to extend the macrocyclic size, the geometrical parameters of *o*-S<sub>2</sub>O with cyclophane group are longer than those of [9]aneS<sub>2</sub>O. R<sub>S1,S2</sub> of 4.01 Å and R<sub>S,O</sub> of ≈ 3.19 Å in *exo*-(*o*-S<sub>2</sub>O) are longer than R<sub>S1,S2</sub> of ≈ 3.96 Å and R<sub>S,O</sub> of ≈ 3.09 Å in *endo*-type, respectively. In experimental result,<sup>17</sup> R<sub>S,O</sub> is similar to that of our result.

Our average R<sub>Pd,Cl</sub> distances (≈ 2.345 Å) in the Pd(L)Cl<sub>2</sub> complexes are longer than those (≈ 2.318 Å) of the experimental results for K<sub>2</sub>PdCl<sub>4</sub> in the solid state.<sup>19</sup> The average R<sub>Pd,S</sub> distances of Pd([9]aneS<sub>2</sub>O)Cl<sub>2</sub> and Pd(*o*-S<sub>2</sub>O)Cl<sub>2</sub> are similar to each other. The R<sub>Pd,S</sub> distance (≈ 2.342 Å) of *endo*-Pd(*o*-S<sub>2</sub>O)Cl<sub>2</sub> is slightly shorter than that (≈ 2.346 Å) of *exo*-Pd(*o*-S<sub>2</sub>O)Cl<sub>2</sub>. This length could be a consequence of enhanced  $\pi$ -back bonding between the sulfur atoms and the central Pd(II) due to  $\sigma$ -donor of the apically coordinated O-atom ligand. Our calculated R<sub>Pd,S</sub> distances of Pd(*o*-S<sub>2</sub>O)Cl<sub>2</sub> are slightly longer than those of the experimental values.<sup>17</sup> The average R<sub>S1,S2</sub> distances (≈ 3.36 Å) in Pd([9]aneS<sub>2</sub>O)Cl<sub>2</sub> is shorter than that (≈ 3.82 Å) in Pd(*o*-S<sub>2</sub>O)Cl<sub>2</sub>. From Pd([9]aneS<sub>2</sub>O)Cl<sub>2</sub> to Pd(*o*-S<sub>2</sub>O)Cl<sub>2</sub>, R<sub>S1,S2</sub> increase. The average distances (R<sub>S1,S2</sub> of ≈ 3.36–3.82 Å) in the complexes are shorter than those (R<sub>S1,S2</sub> of ≈ 3.60–4.01 Å) of the corresponding free macrocyclic ligands. By the complexation between Pd(II) and the bidentate macrocyclic ligands, the macrocyclic frame in the complexes is more rigid and compacted than the corresponding free ligands.

Due to the *exo*- or *endo*-orientation of the oxygen atom, the R<sub>Pd...O</sub> distances in *endo*-Pd(II) complexes are quite different from those of *exo*-Pd(II) complexes. Because of an axial (Pd...O) interaction, the R<sub>Pd...O</sub> distance of *endo*-Pd(II) complexes is shorter than that of *exo*-Pd(II) complexes. The R<sub>Pd...O</sub> distances in *endo*-Pd([9]aneS<sub>2</sub>O)Cl<sub>2</sub> and *endo*-Pd(*o*-S<sub>2</sub>O)Cl<sub>2</sub> are ≈ 2.974 Å and ≈ 2.944 Å, respectively. The R<sub>Pd...O</sub> distances in *exo*-Pd([9]aneS<sub>2</sub>O)Cl<sub>2</sub> and *exo*-Pd(*o*-S<sub>2</sub>O)Cl<sub>2</sub> are ≈ 3.383 Å and ≈ 3.367 Å, respectively. The R<sub>Pd...O</sub> distances of the *endo*-Pd(II) complexes are somewhat shorter than those of *exo*-Pd(II) complexes. The gap of the R<sub>Pd...O</sub> distances between the *endo*- and *exo*-Pd(II) complexes is ≈ 0.5 Å. In crystal structure,<sup>17</sup> the distance (3.38 Å) between the Pd and the O atoms in the *exo*-[Pd(9S<sub>2</sub>O)<sub>2</sub>]<sup>2-</sup> is longer than the sum (3.1 Å) of van der Waals radii for the two atoms,<sup>18</sup> but the distance (2.944 Å) in the *endo*-Pd(*o*-S<sub>2</sub>O)Cl<sub>2</sub> is shorter than that of the van der Waals for the two atoms.

The average atomic charge of the sulfur atoms on the macrocyclic ligand have the positive values (0.02–0.08 au), while, the average atomic charge of the oxygen atoms on the ligand are negative values (-0.65 ~ -0.68 au). Meanwhile, in

the Pd(II) complexes, the atomic charges of Pd(II) have the relatively large positive values (1.24–1.37 au), while, the atomic charges of the chloride, sulfur, and oxygen atoms are negative. The atomic charges of Pd(II) in *exo*-Pd(II) complexes are more positive than those of in *endo*-Pd(II) complexes. The atomic charges of the Cl atoms in *exo*- and *endo*-Pd(II) complexes are similar to each other. The atomic charges of the sulfur and oxygen atoms in *endo*-Pd(II) complexes are different from those of the sulfur and oxygen atoms in *exo*-Pd(II) complexes. That is, the atomic charges of the sulfur atoms on *endo*-Pd(II) complexes are more negative than those of the sulfur atoms on *exo*-types, while, the atomic charges of the oxygen atoms on *endo*-Pd(II) complexes are more positive than those of the oxygen atoms on *exo*-types. In *endo*-Pd(II) complexes with an axial (Pd $\cdots$ O) interaction, the lone pair electron of the oxygen atom as a hard  $\sigma$ -donor donates to Pd(II) and the charge density transfers from Pd(II) to the S-atoms *via*  $\pi$ -acceptors of the empty d-orbitals of the sulfur atom occurs continuously. As a result, the average atomic charges (-0.547 au) of the oxygen atom on the *endo*-Pd(II) complexes are less negative than those (-0.689 au) of the oxygen atom on the *exo*-types. And the average atomic charges (-0.653 au) of the sulfur atom on the *endo*-Pd(II) complexes are more negative than those (-0.589 au) of the sulfur atom on the *exo*-types. The charge variation gap of the oxygen atom between the *exo*- and *endo*-Pd(II) complexes is similar to that of the sulfur atom between the *exo*- and *endo*-types. In the *endo*-Pd(II) complexes, the atomic charges of the oxygen atom are less negative than those of the oxygen atom on the corresponding macrocyclic ligands, while, in the *exo*-Pd(II) complexes, the atomic charges of the oxygen atom are similar to those of the oxygen atom on the corresponding ligands.

Conclusionally, the geometrical structures of [Pd(L)Cl<sub>2</sub>] with bidentate macrocyclic ligands ([9]aneS<sub>2</sub>O and *o*-S<sub>2</sub>O) are optimized to be four coordinate square planar geometry of two sulfur atoms and two chlorides, Pd(II) and the macrocyclic ligands locate at the center and the side plane about the square planar geometry, respectively. When an oxygen atom in the Pd(II) complexes coordinates to Pd(II), more stable conformer (*endo*-dentate Pd(II) complexes) is obtained by an axial (Pd $\cdots$ O) interaction. The geometrical structures of *endo*-Pd(II) complexes with the axial (Pd $\cdots$ O) interaction are more stable than those of the corresponding *exo*-Pd(II) conformers. The atomic charges of Pd(II) on the complexes have positive values, while, the atomic charges of the chloride, sulfur, and oxygen atoms on the complexes are negative. In the *endo*-Pd(II) complexes, the atomic charge of the oxygen atom firstly transfers to Pd(II) *via* the axial (Pd $\cdots$ O) interaction and the charge transfer from Pd(II) to the S-atoms occurs continuously *via*  $\pi$ -acceptors of the empty d-orbitals. As a result, the atomic charges of the sulfur and oxygen atoms of *endo*-dentate complexes are more negative and less negative than those of the sulfur and oxygen atoms of *exo*-types, respectively.

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