Notes

Geometric Features and Electronic Structures of Six-Coordinated Dialkyl and Dithiolate Complexes of Osmium(IV) Porphyrins

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Summary: The majority of six-coordinate d^4 osmium/ruthenium(IV) porphyrin complexes [$M(por)X_2$] have been found to be paramagnetic and have linear X−M−X structural units. However, an exception is found for [Os(por)R_2] and [Os(por)$(SR)_2$] (R = alkyl), which are diamagnetic. While the S−Os−S unit in [Os(por)$(SR)_2$] is linear, the R−Os−R unit in [Os(por)R_2] is found to be significantly bent. In this note, the geometric features and electronic structures of the dialkyl and dithiolate complexes of osmium(IV) porphyrins have been investigated by density functional calculations.

Transition-metal porphyrin complexes have attracted considerable interest because of their relevance to biological systems as well as their catalytic activities in organic oxidations.[1−3] Osmium and ruthenium porphyrin complexes represent a unique class showing the catalytic properties and have been well-studied experimentally.[1−6] In 1994, one of us reported the crystal structure of a dialkylosmium(IV) porphyrin complex, [Os(TTP)$(CH_2SiMe_3)_2$] (TTP = 5,10,15,20-tetra-*p*-tolylporphyrin dianion), which shows a significantly bent C−Os−C unit with an angle of ca. 140° (see **I**; Chart 1).[7] Like other dialkylruthenium(IV) porphyrin analogues,[8−9] this complex was found to be diamagnetic. In contrast, numerous other six-coordinated d^4 osmium/ruthenium porphyrin complexes, [M(por)X_2] (M = Os, Ru; por = porphyrinato dianion; X = monovalent ligands such as alkoxide and halide), do not show the structural distortion and the X−M−X unit in each of these complexes is approximately linear.[10−14] The majority of these approximately linear d^4 metalloporphyrins (see **II**) are found to be paramagnetic, except for [Os(TTP)$(SC_6F_4H)_2$][10] and [Os(OEP)$(SC_6H_5)_2$][15] (OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion), which have exactly linear S−Os−S units and are diamagnetic (see **III**).

The structural distortion found in the dialkylosmium(IV) complex and the diamagnetism observed in the dithiolate complexes are quite unique in comparison with the majority of six-coordinated d^4 Os/Ru porphyrin complexes, which are paramagnetic and have approximately linear X−M−X units. In this note, the electronic reason for the structural distortion in the dialkylosmium(IV) porphyrin complex will be studied through the aid of density functional theory (DFT) calculations. The diamagnetic properties of the dithiolato−osmium(IV) porphyrin complexes will be investigated as well.

Geometry optimizations have been performed on the model complexes [Os(por)$(CH_3)_2$] and [Os(por)$(SCH_3)_2$] at the Becke3LYP (B3LYP) level[16] of density functional theory. For simplicity, the unsubstituted porphyrinato dianion was used in the model calculations. In the B3LYP calculations, LANL2DZ effective core potentials and basis sets[17] were used to describe Os and S, while

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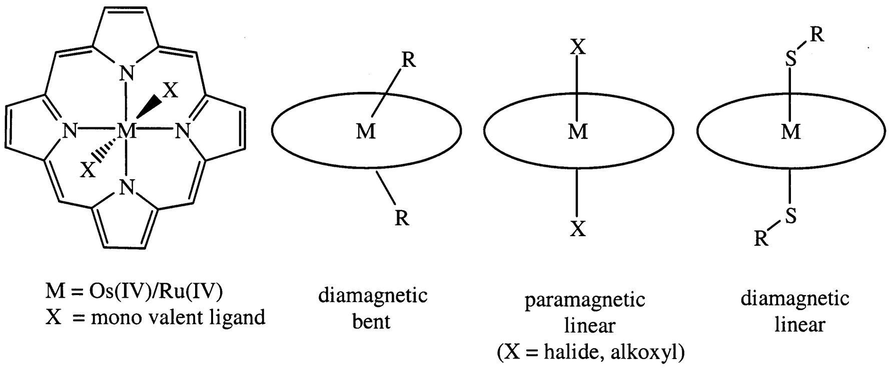
Chart 1



I **II** **III**

the standard 6-31G basis set[18] was used for C and H. Polarization functions were added for atoms directly bonded to the metal center for each model complex: i.e., $\xi_d(S) = 0.421$ and 6-31G* for carbon and nitrogen. All the above calculations were performed with the Gaussian 98 software package.[19] One of the reviewers was concerned that the method used for calculations neglects spin–orbit coupling effects. While the spin–orbit coupling effects have some impact on the spectroscopic properties for compounds containing sixth-row elements, the impact on the bonding and structural aspects is generally very limited.[20] In view of the facts, which will be discussed below, that the experimental structures were well reproduced theoretically and that the predicted ground states are singlet, consistent with the experimental observations for the systems studied here, the spin–orbit coupling effects should not change the qualitative conclusions made in this paper.

The important structural parameters for the two calculated model complexes are shown in Figure 1, together with those from the experimentally characterized [Os(TTP)(CH_2SiMe_3)$_2$] and [Os(TTP)(SC_6F_4H)$_2$] complexes. For the dialkyl complex, the bending feature is well reproduced theoretically. For the dithiolate complex, the S–Os–S unit is calculated to be linear, consistent with the experimental observation. Clearly, the theoretical calculations well reproduce the experimental results.

The calculated model complex [Os(por)(CH_3)$_2$] reproduces the bent structural feature observed in [Os(TTP)(CH_2SiMe_3)$_2$], indicating that the distortion is due to electronic factors rather than steric bulk of the $-CH_2SiMe_3$ groups. For an idealized D_{4h} [M(por)X_2] complex, the "t_{2g}" set of orbitals, commonly found for pseudooctahedral complexes, are expected to split into two levels, in which d_{xz} and d_{yz} are degenerate and higher in energy than the d_{xy} orbital (see Figure 2a) based on the concept of orbital interactions.[21] Complexes with a d^4 electron configuration for the metal centers in such an idealized D_{4h} structure possess a high-spin triplet ($S = 1$) state, having two unpaired d electrons. The dihalo-[12,14] or dialkoxy-[11,13] Ru/Os porphyrin complexes are typical examples of having such an idealized situation. The dialkylosmium complex we are dealing with in this paper is experimentally found to be diamagnetic.[7] In order that [Os(por)R_2] species be diamagnetic, the degenerate pair (d_{xz}, d_{yz}) should split further. The splitting can be achieved only through the bending of the two axial ligands, a kind of first-order Jahn–Teller distortion.[21,22] Figure 2a schematically illustrates the orbital splitting resulted from the axial bending. Various modes of the first-order Jahn–Teller distortion have also been found in many other pseudooctahedral d^4 metal complexes.[23,24] The unique bending mode found in the dialkylosmium(IV) porphyrin complex is due to the rigidity of the porphyrin ring. Figure 2b shows the spatial plots[25] of the highest occupied and the third lowest unoccupied molecular orbitals (HOMO and 3rd

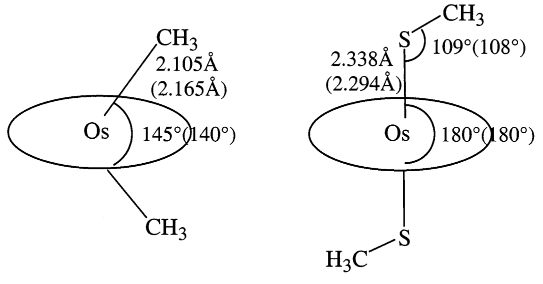


Figure 1. Calculated structures for the model complexes Os(por)(CH_3)$_2$ (left) and Os(por)(SCH_3)$_2$ (right) together with selected experimental structural parameters of Os(ttp)(CH_2SiMe_3)$_2$ and Os(ttp)(SC_6F_4H)$_2$ (given in parentheses). The equatorial porphyrinato dianion (por) planes are represented by ellipses for clarity.

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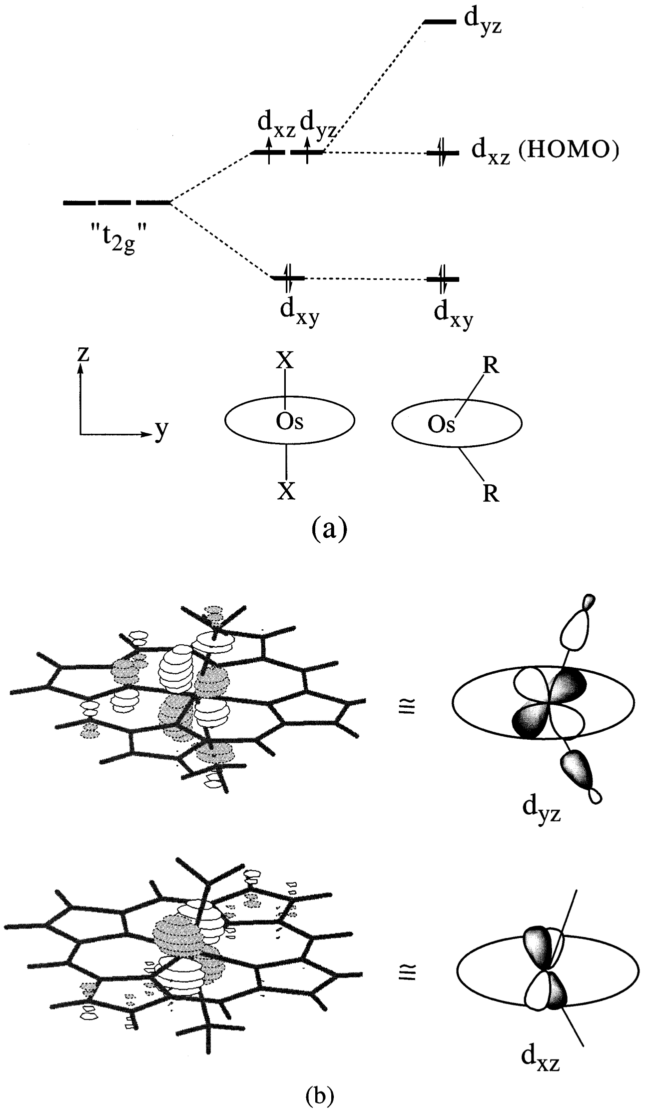

Figure 2. (a) Schematic orbital splitting of the "t_{2g}" set from octahedral (left), to D_{4h} (central), to its axial bending distortion (right). (b) Spatial plots of the d_{yz} (third LUMO) and d_{xz} (HOMO) orbitals for the model complex Os(por)-$(CH_3)_2$. The molecular orbitals were obtained from the B3LYP calculations.

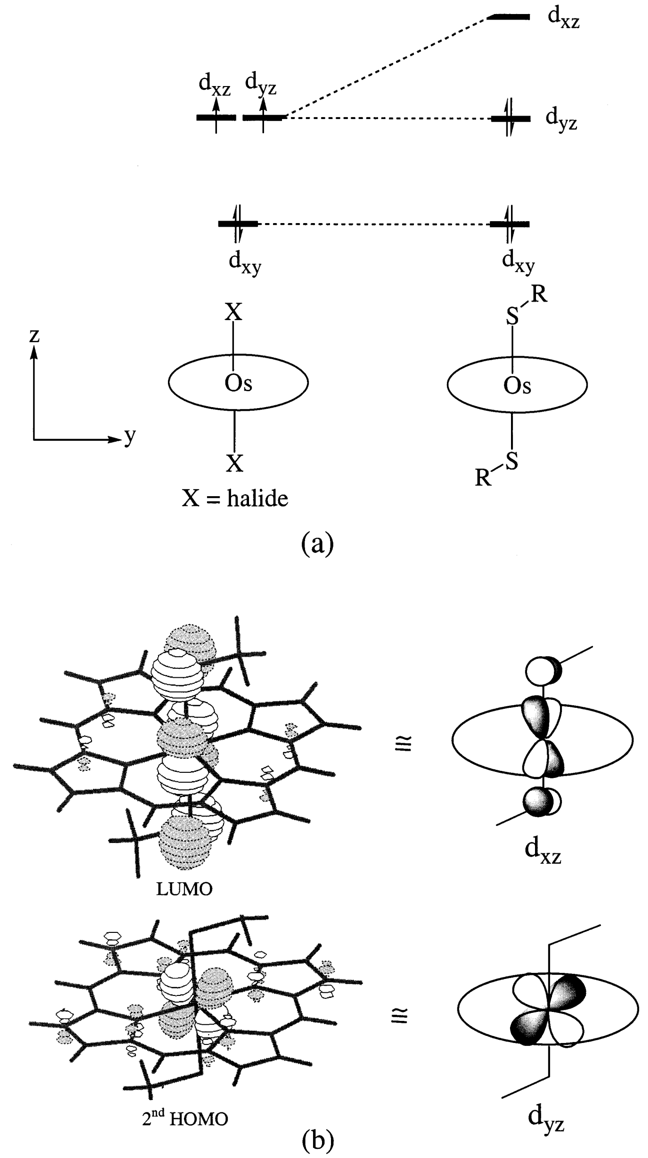

Figure 3. (a) Schematic orbital splitting of the "t_{2g}" set from Os(por)X_2 (X = halide) (left) to Os(por)$(SR)_2$ (right). (b) Spatial plots of the d_{xz} (LUMO) and d_{yz} (second HOMO) orbitals for the model complex Os(por)$(SCH_3)_2$. The molecular orbitals were obtained from the B3LYP calculations.

LUMO) derived from the B3LYP calculations on the [Os(por)$(CH_3)_2$] model complex. The HOMO corresponds to the d_{xz} orbital, while the third LUMO is the d_{yz} orbital, having an antibonding interaction with the two axial methyl ligands. The calculated molecular orbitals are closely related to the qualitative scheme proposed in Figure 2a.

A question arises: why does the dialkylosmium(IV) porphyrin complex not adopt a linear structure and have paramagnetic properties? Calculations on the triplet model complex [Os(por)$(CH_3)_2$] give substantially longer Os−C distances (2.186 Å) and a bent C−Os−C unit with an angle of 160°. The triplet state is calculated to be 16.3 kcal/mol higher in energy than the diamagnetic ground state. These data suggest a strong trans influence of the alkyl ligands. Clearly, we believe that the strong trans influence of the alkyl ligands prevents the adoption of a linear structure for the dialkylosmium(IV) complex. In addition, the strong metal−alkyl bonding interaction can cause an appreciable splitting between the d_{xz} and d_{yz} orbitals through the bending distortion. In the dihalo- or dialkoxyosmium(IV) analogues, the metal (d)−ligand (p) π interactions are comparatively weaker, and thus the bending distortion is expected to cause only a marginal splitting.

For the Os(IV) dithiolate model complex [Os(por)$(SCH_3)_2$], the calculated structure clearly shows a linear S−Os−S unit and the coplanar arrangement of the two dithiolate ligands (see Figure 1). An examination of the molecular orbitals of the model complex in the HOMO−LUMO region shows that the unoccupied d orbital corresponds to d_{xz} instead of d_{yz} found for [Os(por)$(CH_3)_2$]. This unoccupied d_{xz} orbital has significant π^* antibonding character with respect to the Os−SR bonds. This result suggests that the orbital splitting in [Os(por)$(SR)_2$] is due to the metal (d_{xz})−thiolate (p) π interactions instead of the first-order Jahn−Teller distortion observed for [Os(por)R_2]. Similar to the splitting shown in Figure 2a, a schematic orbital splitting can be proposed for the π^* antibonding interaction for [Os(por)(SR)$_2$] (see Figure 3a). The d_{xz} orbital is destabilized through a π^* antibonding interaction with the thiolate ligands. Figure 3b gives the spatial plots[25] of the d_{yz} (occupied) and d_{xz} (unoccupied) molecular orbitals derived from the B3LYP calculations. The d_{yz} orbital corresponds to the second HOMO, while the unoccupied d_{xz} orbital is the LUMO. The destabilization of d_{xz} is a result of the single-faced π-donor properties of thiolate ligands. The d_{xz} orbital can be considered as stabilizing the p orbitals that accommodate the p lone pairs on SR$^-$ through a d−p π-bonding interaction. Such a π-bonding interaction is further enhanced with the coplanar arrangement of the two SR$^-$ ligands. In other words, the coplanar arrangement causes a big $d_{xz}-d_{yz}$ splitting, resulting in the diamagnetism for [Os(por)(SR)$_2$]. The diamagnetism of diamido osmium(IV)/ruthenium(IV) porphyrins has also been related to metal (d)−nitrogen (p) π bonding interactions.[26]

As mentioned in the Introduction, unlike the dithiolate analogues, [Os(por)(OR)$_2$] species are paramagnetic with linear RO−Os−OR units. The difference between the two complexes can be conveniently related to the weaker Os−OR π-bonding interaction compared with that of Os−SR. The strong Os−SR π interaction is due to the diffuse nature of the 3p orbitals of sulfur. In addition, the angle flexibility of the Os−O−C unit observed for [Os(por)(OR)$_2$] contributes to the small splitting between the d_{xz} and d_{yz} orbitals. In an extreme case when the Os−O−R linkage is linear, the d_{xz} and d_{yz} orbitals remain degenerate and no splitting occurs. The majority of [Os(por)(OR)$_2$] species have Os−O−C angles greater than 126°, whereas the Os−S−C angles in [Os(por)(SR)$_2$] are found to be around 107°.[10,11,15]

In summary, we have demonstrated that simple MO analyses, which are well covered in textbooks,[21] can be used to explain the electronic structures of complicated organometallic systems. The bent structural feature found in the dialkylosmium(IV) porphyrin complex is a result of first-order Jahn−Teller distortion. The instability of a paramagnetic (triplet) [Os(por)R$_2$] with a linear C−Os−C unit is related to the strong trans influence of the alkyl ligands. For the osmium(IV) dithiolate complexes [Os(por)(SR)$_2$], the stronger Os(d)−S(p) π interactions cause a large splitting between two of the three "t_{2g}" orbitals when the two dithiolate ligands are coplanar. The large splitting between the d orbitals results in diamagnetic properties for the complexes. For the dialkoxyosmium(IV) analogues, the weak Os−OR π interactions as well as large Os−O−C angles result in a relatively small d orbital splitting, and therefore, paramagnetic properties are observed.

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