

Complexes Formation of Porphyrin Derivatives with Lead: Preliminary Computational Study of Porphyrin as Analytical Reagent

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Abstract:

Interaction of three cationic porphyrins: *meso*-tetrakis (*N*-methylpyridinium-4-yl) porphyrin (H₂TMPyP), *meso*-tetrakis (1,3-dimethylimidazolium-2-yl)porphyrin (H₂TDMIImP), and *meso*-tetrakis(1,2-dimethylpyrazolium-4-yl) porphyrin (H₂TDMPzP) with lead have been performed computationally using DFT method. DFT global chemical reactivity descriptors (electronic chemical potential, chemical hardness, and electrophilicity) were calculated and used to predict their relative stability and reactivity. The structural parameters such as bond length (Pb-NPh and Pb-PPh) and angle between lead metal with porphyrin plane (Pb-plane) were also calculated. It showed that the electronic chemical potential of Pb-TDMIImP, Pb-TMPyP, and Pb-TDMPzP were increase, while their chemical hardness were 0.050, 0.044, and 0.047, respectively. The electrophilicity of Pb-TDMIImP, Pb-TMPyP, and Pb-TDMPzP were 2.520, 2.415, and 2.088. The angle between lead metal with porphyrin plane showed that lead metal is not likely to stay inside the porphyrin core, but it out of the porphyrin plane. In conclusion, complex of H₂TDMIImP with lead is the most stable and the least reactive toward accepting electrons with the electronic chemical potential, chemical hardness, and electrophilicity were -0.502, 0.050, and 2.520 (au), respectively, and 27.87° for Pb-plane.

Key words: *Analytical reagent, metalloporphyrin, chemical hardness, DFT, electronic chemical potential, electrophilicity*

Introduction

Porphyrin is a naturally occurring macrocyclic compound, which has attracted considerable attention because its role in life and ubiquitous in natural systems, beside that, it has prospective application in analytical chemistry. The large molar absorption coefficient and high stability of porphyrin, make it applicable for separating various kinds of metal ions. Lead is the most abundant of the heavy metals in the Earth's crust [3].

The metalloporphyrin formation is one of the important processes in analytical point of view. The porphyrin core is tetradentate ligand that has space to coordinate with various kinds of metal ion. Depending on their size, charge, and spin multiplicity, metal ion can fit into the porphyrin core forming regular metalloporphyrins or just sit on top of the molecule forming sitting-atop metalloporphyrins. Most of the natural metalloporphyrins are regular type when the metal ions have ionic radii in the range of 55-80 pm, while if the metal ions are large, that have ionic radii over 80-90 pm, they are located out of the ligand plane forming sitting-atop metalloporphyrins [1].

Ionic radii of lead (Pb²⁺) is 118 pm [2]. Exposure and uptake of lead in nature are increase because lead is widely distributed in the environment [3]. Exposure of metallic lead is still problem in some country and occurs mainly orally through food and water. Lead contamination in food and water can cause adverse effects on human health such as decreased activity of enzymes and kidney function, and also causes neuromuscular disorder [4].

Therefore, monitoring of lead contamination is an important concern and porphyrin is the prospective ligand to be used as analytical reagent for metal analysis.

Water soluble *meso*-substituted porphyrins have very high sensitivity as chromogenic reagents for detection metal ion because they have Soret bands with large molar absorptivity (10⁵) and easily handled than water insoluble reagents. Cationic porphyrin is a potential *meso*-substituted porphyrin because its water soluble [5].

In the present study, interaction of three *meso*-substituted cationic porphyrin, *meso*-imidazolium (H₂TDMIImP), *meso*-pyrazolium (H₂TDMPzP), and *meso*-pyridine (H₂TMPyP) with lead (Figure 1) will be observed based on structural and electronic properties using DFT. DFT global chemical reactivity descriptors, that is chemical hardness (η), electronic chemical potential (μ), and electrophilicity (ω) are calculated and used to predict their relative stability and reactivity of the complexes. The structural parameters such as bond length (Pb-NPh and Pb-PPh) and angle between lead metal with porphyrin plane (Pb-plane) were also calculated.

Experimental

The computations were performed using Gaussian 09 and GausView 05. All the geometrical optimizations were carried out using DFT B3LYP level with 6-31G basis set for free-base porphyrin and LANL2DZ basis set for metalloporphyrin. DFT global chemical reactivity descriptors are calculated following this equation [6]:

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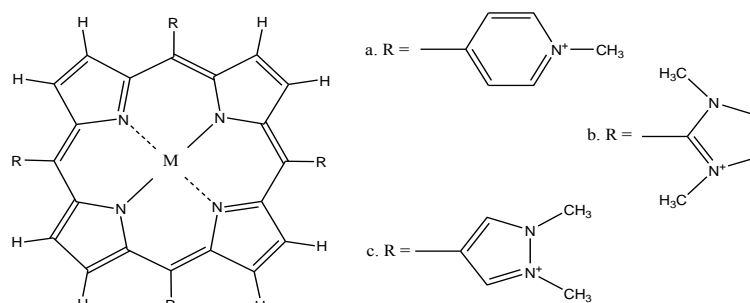


Figure 1. Chemical structures of (a) H₂TMPyP, (b) H₂TDMIImP, (c) H₂TDMPzP with M = H₂ (for free-base porphyrin) and Pb²⁺.

Electronic chemical potential:

$$\mu = (E_{\text{homo}} + E_{\text{lumo}}) / 2 \quad (1)$$

Chemical hardness:

$$\eta = (E_{\text{lumo}} - E_{\text{homo}}) / 2 \quad (2)$$

Electrophilicity:

$$\omega = \mu^2 / 2 \eta \quad (3)$$

Results and Discussion

All of parameter (bond lengths, angle between lead metal with porphyrin plane and DFT global chemical reactivity descriptors) were calculated after optimized geometries were obtained. The molecule was optimized to get most stable conformation which shown with the lowest energy. Table 2 in first row showed that complex of Pb-TDMIImP has lower energy. It indicates that Pb-TDMIImP complex is more stable than others because it need more energy to break the bonds in the molecule.

The structural parameter such as bond lengths and the angle between lead metal with porphyrin plane were calculated. Figure 2 shows the visualization of complexes and the results showed in Table 1.

Table 1. Calculated bond length and angle of three Pb-porphyrin complexes

Parameters	Pb-TMPyP	Pb-TDMIImP	Pb-TDMPzP
Pb-NPh (Å)	2.370	2.370	2.366
Pb-PPh (Å)	1.215	1.108	1.101
∠Pb-Plane (°)	30.840	27.870	27.730

Pb-NPh : the average bond length of lead-porphyrin nitrogen.

Pb-PPh : the bond length of lead and porphyrin plane.

∠Pb-Plane: the angle between lead metal with porphyrin plane.

All of porphyrin derivatives have a similar bond length (Pb-NPh and Pb-PPh) and angle (Pb-Plane), indicating that metal ion is far away from the porphyrin plane. As

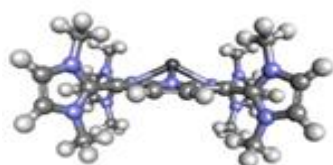
shown in Figure 2, Pb²⁺ ion is not stay inside in the porphyrin core but it outside of the porphyrin plane. It occurs due to ionic radii of Pb²⁺ is too large (118 pm), over 80-90 pm. The porphyrin core does not have enough space to accommodate the metal ion, so they are located out of the ligand plane forming sitting-atop metalloporphyrins. This complex is kinetically labile and strongly deviates from those of regular metalloporphyrins [1].

The rate of formation of regular metalloporphyrins is much slower than the sitting-atop complexes because of the inflexibility of porphyrins. Moreover, the distortion in an sitting-atop complex can cause two diagonal pyrrolic nitrogen be easily displaced by proton because it is more accessible on the other side of the ligand [1,7].

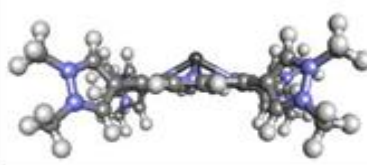
DFT global chemical reactivity descriptors are used to describe structural and electronic properties of lead-porphyrins complexes. The parameter can be calculated using orbital theory approaches by measuring the HOMO and LUMO energy. HOMO and LUMO energy was calculated on optimized. Figure 3 shows the visualization of HOMO and LUMO contour surface of lead-porphyrin complexes as summarized in Table 2.

Table 2. Global chemical reactivity descriptors of Pb-porphyrins complexes

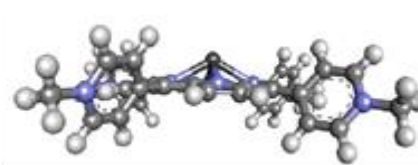
Parameters	Pb-TDMIImP	Pb-TMPyP	Pb-TDMPzP
E (au)	-2207.308	-2138.341	-2207.226
HOMO (au)	-0.551	-0.504	-0.490
LUMO (au)	-0.452	-0.417	-0.396
μ (au)	-0.502	-0.461	-0.443
η (au)	0.050	0.044	0.047
ω (au)	2.520	2.415	2.088



Pb-TDMIImP



Pb-TDMPzP



Pb-TMPyP

Figure 2. Optimized structure of three Pb-porphyrin complexes.

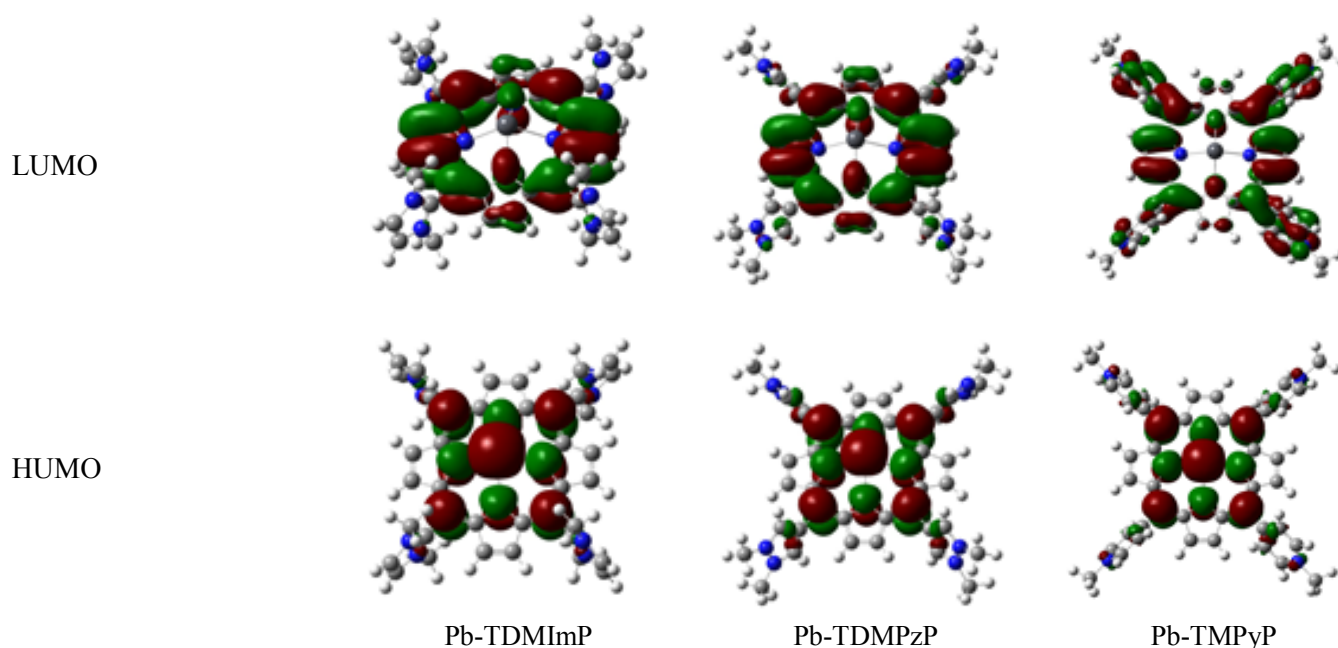


Figure 3. HOMO and LUMO contour surface of lead-porphyrin complexes.

The results (Figure 3) showed that electron distribution of complex porphyrin with lead is populated around porphyrin core. It showed that interaction of porphyrin with lead is occurs in porphyrin core through interaction between nitrogen-pyrol with positive charge of Pb^{2+} .

Electronic chemical potential is describes electronegativity of molecule that measure the escaping tendency of electrons from an equilibrium system [8]. This parameter determined using equation:

$$\mu = (I + A) / 2 \quad (4)$$

where I and A are the ionization energy and electron affinity of the electron system (neutral or charged) studied. As an approximation, the ionization energy and electron affinity can be replaced by the HOMO and LUMO energy, respectively as in equation (1) [6]. The results (Table 2), showed that Pb-TDMPzP had the smallest electronic chemical potential than the others. It suggests that Pb-TDMPzP complex is the least reactive or more stable because the complex will retain the electron to escape from system.

Chemical hardness is resistance of the chemical potential to change in the number of electrons that correlated with the stability and reactivity of a chemical system [9]. Chemical hardness was calculated as expressed in equation (2) which indicating that hardness is related to the energy gap between occupied and unoccupied orbitals [6]. Hard molecules have a large HOMO-LUMO gap that means large excitation energies to the manifold of excited states [10]. The larger the hardness, the harder and more stable molecule. As summarized in the table 2, Pb-TDMPzP is harder and less reactive than others.

Electrophilicity is a reactivity index that combining electronic chemical potential and hardness, as shown in equation (3), that showed the propensity of electrophilic attack [8]. It is measure of the capacity of species to accept electrons. The trend in electrophilicity is decrease from Pb-TDMPzP, Pb-TMPyP, Pb-TDMPzP. The smaller electrophilicity suggest that the system become less reactive toward accepting electrons [11]. Lead-porphyrin complexes are stable if they have smaller electrophilicity because metal ion can not easily displaced. Thus, Pb-TDMPzP is less reactive in electrons-accepting reaction.

Conclusions

The stability of complex lead-porphyrin is affected by the ionic radii of lead metal, and the metal is out of porphyrin plane. Based on DFT global chemical reactivity descriptors, Pb-TDMPzP had the smallest electronic chemical potential (μ) value, largerst chemical hardness (η) and electrophilicity (ω). Thus, Pb-TDMPzP complex is more stable than two other complexes.

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