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Following nature—Theoretical studies on factors modulating catalytic activity of porphyrins

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Abstract

The aim of the present density functional theory (DFT) study is to investigate how the modifications in the structure of porphyrin-based complexes could change their catalytic properties, taking as examples heme and Fe and Mn porphyrins. As factors determining catalytic activity, the following parameters are chosen: the charges on the metal ion and the O_2 ligand, lengths and bond orders of the metal–oxygen and oxygen–oxygen bonds, and dioxygen-binding energies. The results indicate that the naturally occurring heme–O_2 complex should be more active than the dioxygen iron(II) porphyrin, because the bound dioxygen has more nucleophilic character and would be more susceptible to scission. The exchange of iron to manganese would improve nucleophilicity of the O_2 molecule and weaken the metal-O_2 bond. Finally, iron(II) seems to be a better choice for dioxygen binding than iron(III).
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1. Introduction

A direct consequence of the ability of the heme group to bind small ligands (including molecular oxygen) is its role in enzymatic oxidations. The involvement of heme in these processes inspired chemists to profit from these naturally occurring catalysts and employ them into industrial processes. In order to do so, the core of the heme group, that is the porphyrin ring with the central atom, has been selected. Reduced in such a way complexes are the bases for the selective oxidation catalysts in homogeneous phase [1]. Numerous studies have shown that small structural differences among metalloporphyrins allow fine tuning of their activity and selectivity. Using various transition metals in different oxidation states as central ions could modify the catalytic performance of metalloporphyrins. It has been also found that introduction of electron-donating or electron-withdrawing substituents on the porphyrin ring peripheries as well as using of different axial ligands may modify the catalytic performance of the studied compounds [2].

The calculations presented in this paper are aimed to attempt how the above-mentioned modifications could change the electronic and geometric structure of the investigated complexes. In order to study the influence of modification, heme and the iron and manganese porphyrins are taken as examples. The iron ion is chosen for the sake of comparison with the naturally occurring porphyrins. The choice of the second metal is based on the experimental observable that manganese porphyrin complexes are generally preferred for hydrocarbon oxidation as they often perform better than the iron systems in terms of rates and efficiency [1]. Additionally, the complexes of the above-mentioned metal atoms are believed to cause less damage to environment than of other transition metals.

Here the stress is put on the electronic and geometric parameters that may affect the catalytic performance of the examined structures. As those, the charges on the metal ion and the O_2 ligand and other factors describing the metal–oxygen and oxygen–oxygen bonds (lengths and bond orders) are taken. Additionally, the O_2-binding energies in different complexes are compared. While doing this study we are aware of the fact that not only the electronic properties of the active site (the heme group or the porphyrin complex), but also the external conditions such as the protein environment, solvent, tempera-

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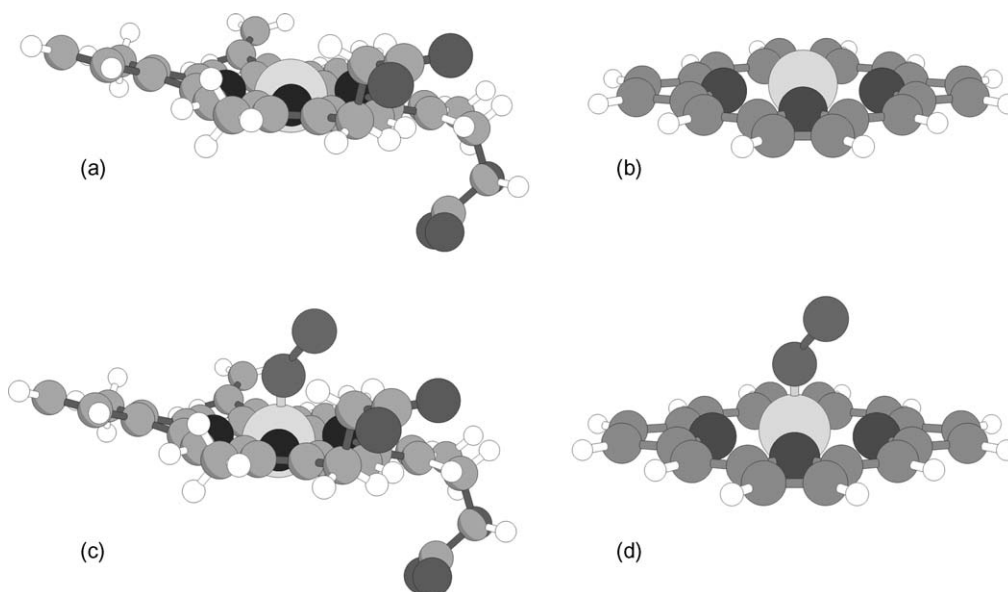 ncwitko@cyf-kr.edu.pl (M. Witko).

Fig. 1. Models of structures investigated in this paper: $[Fe(PPIX)]^{2-}$ (a); [MP], M = Fe, Mn (b); $[Fe(PPIX)O_2]^{2-}$ (c); $[MPO_2]$, M = Fe, Mn (d).

ture, etc., affect the catalytic behavior. However, it is our belief that the examination of the electronic parameters of the most active part of the catalyst would allow for the deeper understanding of its reactivity and would help in rational catalyst design.

The reasons for the choice of the parameters to be selected follow from their use in discussing catalytic properties. The charge accumulated on a fragment of the catalyst may indicate its acid–base properties. More positive the moiety, more acidic in Lewis sense it is. Consequently, the fragment is more electrophilic and would react with electron rich compounds more easily. Inversely, the negative charge accumulated on the fragment would increase its Lewis base behavior (the system will be more nucleophilic) and thus enhance its reactivity towards electron poor species. In case of catalysts based on the porphyrin system, the charge accumulated on the coordinated dioxygen species is essential. This is mainly due to the fact that it is the oxidizing agent that takes part in catalytic reactions, usually via nucleophilic attack towards protons from organic substrates [1]. Another key parameter here would be the charge accumulated on the oxygen atom that is less encumbered and, as a consequence, may react more easily. This is usually the outer oxygen one.

Moreover, in view of the fact that oxidation processes usually require the dioxygen-binding step and its (sometime partial) incorporation into a substrate, the parameters of the $M-O_2$ and O–O bonds are vital for the catalysis. The elongation and the weakening of the O–O bond facilitate all processes that proceed via the rupture of this bond. Similarly, if the $M-O_2$ bond is weaker and longer the oxygen molecule may be easier transferred to the reactant. Therefore, a good catalyst should be characterized by moderate O_2-binding energy and ability to activate that is to weaken and elongate O–O bond.

2. Experimental–theoretical method and model

As theoretical models, the following complexes: [Fe (PPIX)]$^{2-}$, FeP, MnP (where PPIX = protoporphyrin IX, P = porphyrinato ligand), together with $[Fe(PPIX)O_2]^{2-}$, FePO$_2$, FePClO$_2$, and MnPO$_2$ (resulting from their reactions with dioxygen) are selected. The studied structures are presented on Fig. 1.

The investigated systems are modeled by means of density functional theory (DFT) method using StoBe [3] program code. The choice of the methodology follows from the fact that it is widely used to study transition metal complexes as well as catalytic reactions of both homogeneous and heterogeneous types. The Kohn–Sham orbitals are described by extended all-electron basis sets of the Gauss type orbitals [4]. The geometry of the porphyrin ring is frozen during calculations assuming that it is not affected by the coordination of the oxygen molecule. As a consequence, the geometry optimization procedure is applied exclusively to central metal atoms and the molecular oxygen within LDA–VWN functional [5]. The electronic parameters of the system are then recalculated with GGA–RPBE functional [6,7]. Charges are extracted from Mulliken population analysis [8] and as bond orders Mayer bond indices are taken [9]. One should mention here, that in literature many population analyses exist, among which Mulliken analysis is one of the most often used, what is the reason for our choice. By using this population analysis, however, we are aware of the fact that this must be taken with caution. On the one hand, it can provide very useful information on the electron distribution in a molecule and may indicate the electron transfers between different parts of a system. On the other hand, it contains some drawbacks, among which the following are the most serious: the dependence on the basis set employed and the arbitrary partitioning of the electron density into individual orbitals. Therefore, the interpretation of

$$[FePPIX]^{2-} \longrightarrow [FeP] \longrightarrow [MnP]$$
$$\downarrow \qquad\qquad \downarrow \qquad\qquad \downarrow$$
$$[FePPIXO_2]^{2-} \longrightarrow [FePO_2] \longrightarrow [MnPO_2]$$
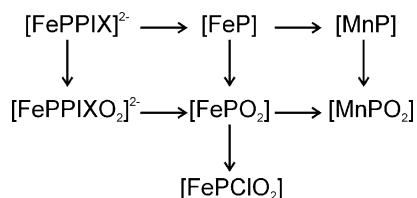$$\downarrow$$
$$[FePClO_2]$$

Fig. 2. Modifications investigated in the present paper.

its results may only be qualitative, as it cannot reproduce correctly the amount of charge transferred during the formation of a molecular complex.

3. Results and discussion

In the following, the changes of the geometry and electronic structures between studied systems are discussed and interpreted with the stress put on the parameters relevant for catalysis. First, the effect of the changes in the porphyrin ring substituents (from protoporhyrin IX to the bare porphyrinato ligand) is examined in O_2-free complexes (in Section 3.1), followed by the investigation of their adducts with dioxygen (in Section 3.2). Next, in the analogous way the influence of the type of the central metal ion (change form Fe to Mn) is studied (in Sections 3.3 and 3.4, respectively). Finally, the impact of the central metal oxidation state (and inclusion of the additional axial ligand) is scrutinized in Section 3.5. All discussed modifications are schematically presented on Fig. 2.

3.1. Influence of the porphyrin ring substituents ($[Fe(PPIX)]^{2-} \rightarrow [FeP]$)

The discussion is started with a comparison between $[Fe(PPIX)]^{2-}$ and $[FeP]$, which is due to the fact, that in the biological systems the oxidation processes are catalyzed by the heme species, while chemists use the unsubstituted porphyrin skeleton as a base for the catalyst.

The total multiplicity of the $[Fe(PPIX)]^{2-}$ complex is equal to 3. The same system calculated as a singlet is characterized by the total energy higher by 0.47 eV than the triplet state. The iron ion is positively charged and the atomic charge on the iron ion accumulated on amounts to 0.67. The negative charge of the PPIX ring (-2.67) results from its anionic character as well as from the presence of unprotonated propionic substituents.

For the FeP complex three different states characterized by different multiplicities (1, 3, 5) have been examined. The structure in which there are two unpaired electrons (triplet) has the lowest total energy. In this system the atomic charge accumulated on the iron ion is equal to 0.68 and on the porphyrin ligand to -0.68.

The comparison of the central ion charge in both structures shows that while going from the $[Fe(PPIX)]^{2-}$ complex to the $[FeP]$ system, the Fe charge remains constant ($\Delta q = 0.01$). Thus, the electrophilicity of the central atom is comparable. The difference in charging of the tetrapyrrolic ligand is a consequence of the presence of two propionic acid groups in heme.

Table 1
The main parameters of the studied dioxygen adducts

Complex	$[Fe(PPIX)O_2]^{2-}$	$[FePO_2]$	$[MnPO_2]$	$[FePClO_2]$
$E_b^{O_2}$	−60.2	−55.2	−48.9	19.2
R (Å)				
M–O	1.73	1.69	1.7	1.75
O–O	1.28	1.26	1.27	1.25
Bond orders (B.O.)				
M–O	1.08	1.20	1.05	0.94
O–O	1.17	1.25	1.29	1.15
Charges (q)				
M	0.66	0.48	0.69	0.13
O1	−0.08	−0.01	−0.08	−0.03
O2	−0.16	−0.15	−0.16	−0.12
O_2	−0.24	−0.16	−0.24	−0.15
PPIX/P	−2.34	−0.32	−0.45	0.15

Energies are in kJ/mol.

3.2. Influence of the porphyrin ring substituents on dioxygen complexes ($[Fe(PPIX)O_2]^{2-} \rightarrow [FePO_2]$)

The parameters of both $[Fe(PPIX)O_2]^{2-}$ and $[FePO_2]$ complexes are listed in Table 1.

The $[Fe(PPIX)O_2]^{2-}$ system is diamagnetic. The charge accumulated on the iron ion amounts to 0.66, while on the dioxygen ligand to -0.24. The negative charge of the dioxygen ligand is not equally distributed between two oxygen atoms, the charge on the outer oxygen atom (in Table 1 referred to as O2), is twice as high ($q^{O2} = -0.16$) as on the oxygen atom connected with the iron ion (in Table 1 referred to as O1, $q^{O1} = -0.08$). The Fe–O distance amounts to 1.73 Å, and this bond order to 1.08. The O–O bond is as long as 1.28 Å (that is more by 0.06 Å than in the isolated O_2) and the bond order equals 1.17 (that is lower by 0.70 than in the free O_2). The dioxygen-binding energy is equal to -60.2 kJ/mol.

For the $[FePO_2]$ system two geometries of the O_2 ligand coordination are examined, side-on and end-on. The one with dioxygen bound end-on to the iron ion has lower total energy by 0.88 eV. The end-on complex is diamagnetic. The iron ion charge amounts to 0.48, while the total charge on the dioxygen ligand to -0.16. Similarly to the previous complex, the charge of the outer oxygen atom is mainly contributing to the total charge observed on the O_2 species. Dioxygen forms a bond with the iron ion of the length of 1.69 Å and of bond order equal to 1.20. The O–O distance amounts to 1.26 Å and the O–O bond order to 1.25, while in the isolated O_2 molecule these values are 1.22 and 1.87 Å, respectively. The O_2 species binding energy equals to -55.2 kJ/mol.

The comparison of the oxygen complexes of the above-mentioned compounds (Table 2, the first column) reveals that both structures differ more than their dioxygen-free forms. The change of the PPIX ring for the porphyrin results in the reduction of the central metal ion ($\Delta q = -0.18$). Additionally, the O_2 ligand bound to the porphyrin ring is more positively charged than bound to the heme complex. The negative charge accumulated on the O_2 species is higher by 0.08 in FeP that in $[Fe(PPIX)]^{2-}$.

Table 2
The differences in the main parameters of the studied dioxygen adducts

Modification	$[Fe(PPIX)O_2]^{2-} \rightarrow$ $[FePO_2]$	$[FePO_2] \rightarrow$ $[MnPO_2]$	$[FePO_2] \rightarrow$ $[FePClO_2]$
$\Delta E_b^{O_2}$	5	6.3	74.4
ΔR (Å)			
M–O	−0.04	0.01	0.06
O–O	−0.02	0.01	−0.01
ΔB.O.			
M–O	0.12	−0.15	−0.26
O–O	0.08	0.04	−0.1
Δq			
M	−0.18	0.21	−0.35
O1	0.07	−0.07	−0.02
O2	0.01	−0.01	0.03
O_2	0.08	−0.08	0.01
PPIX/P	2.02	−0.13	0.49

Energies are in kJ/mol.

Noteworthy, the negative charge on the outer oxygen atom is also higher in $[Fe(PPIX)O_2]^{2-}$. This has serious implications regarding catalysis and is attributed to the fact that the outer oxygen suffers less from steric hindrances than the one connected to the central atom and, as a consequence, is the one that reacts with a substrate. Therefore, it is not only the nucleophilicity of the whole group that counts, but also the difference in nucleophilicity of the two oxygen atoms and the higher negative charge of the outer oxygen atom. The O–O bond is shortened by 0.02 Å in porphyrin complex and their bond order is increased by 0.08. Taking into account the fact that the activation of dioxygen is expressed by the elongation and weakening of the O–O bond as well as by the negative charge accumulated on the O_2 moiety one can see that $[Fe(PPIX)]^{2-}$ complex is able to activate dioxygen stronger than [FeP].

Moreover, on going from heme to porphyrin complex the Fe–O bond is shorter by 0.04 Å and has lower covalency (bond order diminishes by 0.12) in the porphyrin adduct than in $[Fe(PPIX)O_2]^{2-}$. This indicates that the bond between the iron atom and dioxygen is weaker in $[FePO_2]$ than in the similar complex formed by the heme group. The weaker the bond, the easier is to rupture it, and incorporate the O_2 species into a substrate. On the other hand, as can be seen from the differences in the O_2-binding energies, the O_2 molecule is stronger bound to the heme complex by only 5 kJ/mol than to the porphyrin one. This difference is too small to allow drawing any definite conclusions.

3.3. Influence of the type of the central metal ion ([FeP] → [MnP])

The [FeP] system has already been described in Section 3.1. For the [MnP] complex, three multiplicities of the system have been considered, 2, 4, and 6. Our calculations show that the state with three unpaired electrons (quartet) has the lowest total energy. In this complex the charge accumulated on the manganese ion amounts to 0.83.

It is seen that if the manganese atom is used instead of the iron one, the central ion charge is more positive and, consequently, the porphyrin ring is more negative. The difference in charging of the central metal ion amounts to 0.15. One may thus conclude that the manganese ion constitutes more electrophilic center for a catalytic reaction.

3.4. Influence of the type of the central metal ion on dioxygen complexes ([FePO₂] → [MnPO₂])

Next, the comparison is made between the oxygen adducts of the two complexes, namely $[FePO_2]$ and $[MnPO_2]$. The main structural parameters describing both structures are collected in Table 1.

The detailed discussion of the structural parameter of the $[FePO_2]$ complex is done in Section 3.2.

Performed computations of the manganese(II) complexes with dioxygen bound either end-on or side-on shows that in the studied complex the dioxygen prefers end-on geometry. In this structure the charge on the manganese ion equals to 0.69. The axial ligand is negatively charged, the charge accumulated on the O1 species amounts to −0.24, two third of which is accumulated on the outer oxygen atom (O_2). The charge on the porphyrin ligand is equal to −0.45.

The O_2 ligand is distant by 1.70 Å from the central ion. This bond order amounts to 1.05. The O–O bond is as long as 1.27 Å and is elongated by 0.05 Å in comparison with the isolated O_2 species, its bond order equal to 1.29, that is less by 0.58 than similar bond in free O_2. The dioxygen-binding energy amounts to −48.9 kJ/mol.

In the resulting O_2-adduct manganese ion has higher positive charge (by 0.21) than the iron ion in the porphyrin system (see Table 2, the second column). The oxygen molecule acquires more negative charge, thus becomes more nucleophilic. The difference in charging of the O_2 species is equal to −0.08. Nevertheless, the charging of the outer oxygen atom is comparable in both complexes ($\Delta q = -0.01$).

There are almost no changes in metal–oxygen or oxygen–oxygen bonds lengths while going from $[FePO_2]$ to $[MnPO_2]$ system. The O_2-binding energy is lower only by 6.3 kJ/mol in the manganese porphyrin than in the iron one. Taking into account all the above-mentioned parameters one may conclude that the molecular oxygen is slightly weaker bound by [MnP] than [FeP]. Consequently, the $[MnPO_2]$ would be of a bit greater significance to catalysis than $[FePO_2]$, but the differences between the two structures are rather small.

3.5. Influence of the Metal Ion Oxidation State ([FePO₂] → [FePClO₂])

Another interesting modification of the studied system is the change of the oxidation states of the central atom, which may influence the geometric and electronic structures of the porphyrin complexes, in particular its oxygen-binding properties. In order to examine the modifications induced by the change of the oxidation sate of the central metal ion, the iron porphyrin complex is chosen. In the resulting structure, it was decided

that the additional positive charge resulting from iron(III) oxidation state is compensated by introducing a negatively charged ligand Cl^- in the trans position with respect to dioxygen. One should stress here, that due to the construction of the model, the observed changes should not be attributed only to the effect of the metal oxidation state, but also to the presence of the additional axial ligand. Table 1 gathers the calculated parameters of the resulting $[FePClO_2]$ system.

In the $[FePClO_2]$ structure the charge on the iron ion amounts to 0.13, whereas on the dioxygen ligand to -0.15. Similar to the previously described dioxygen adducts, the majority of the negative charge is located on the outer oxygen atom (O2). The formation of the $[FePClO_2]$ complex from isolated $[FePCl]$ and O_2 costs 19.2 kJ/mol. The Fe–O bond of 1.75 Å, which bond order amounts to 0.94, characterizes the resulting complex. The O–O bond length (1.25 Å) is larger by 0.03 Å than in the free O_2 molecule. This bond order equals to 1.15, which is less by 0.72 than in isolated O_2. Both, the observed elongation of O–O bond as well as the lowering of this bond order suggest its activation.

The differences induced by the change of the central atom oxidation state from II to III in its adduct with the molecular oxygen as well as the introduction of the additional axial ligand (Cl^-) to the system are listed in the third column of Table 2. Upon this process the central ion is reduced ($\Delta q = -0.35$), but the molecular oxygen preserves its charge ($\Delta q = 0.01$). Although the O–O bond length is not changed ($\Delta R = -0.01$ Å), the O–O bond order is slightly increased ($\Delta B.O. = 0.10$) showing that the $[FePCl]$ system might stronger activate the O–O bond. The metal–oxygen bond is elongated by 0.06 Å what is reflected by the decrease of its bond order by 0.26. With this respect, the molecular oxygen is weaker bound to Fe(III) than to Fe(II). This observation is further supported by the O_2-binding energies in both complexes. While O_2 binding to $[FeP]$ be exoenergetic, in case of $[FePCl]$ the same process requires 19.2 kJ/mol introduced to the system. This is in line with the observation that in biological systems it is Fe(II) that effectively binds dioxygen.

The difference in the binding energies of the O_2 species amounts to 74.4 kJ/mol.

4. Conclusions

One should stress that the changes of the porphyrin ring substituents (from protoporphyrin IX to porphyrinato ligand), as well as the central atom (type of metal as well as its oxidation state) induces changes in the charge accumulated on the metal ion, in the bond orders of metal–oxygen and oxygen–oxygen bonds, and in the O_2-binding energies. As a consequence, the catalytic behavior of the studied species may be changed. The results of the calculations show that nature would do better with $[Fe(PPIX)]^{2-}$ than chemists with the basic iron(II) system i.e. $[FeP]$. The comparison of the parameters of the oxygen molecule bound to $[Fe(PPIX)]^{2-}$ and $[FeP]$ demonstrates that the O_2 species of the $[Fe(PPIX)O_2]^{2-}$ system would be more nucleophilic and will be more susceptible to scission. The exchange of iron to manganese would improve nucleophilicity of the bound molecular oxygen as well as weaken the metal–dioxygen bond. Finally, iron(II) seems to be a better choice for dioxygen binding than iron(III), however, the latter activates better the O_2 species.

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