

From activation of dioxygen to formation of high-valent oxo species: Ab initio DFT studies

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Received 21 March 2007; received in revised form 19 May 2007; accepted 21 May 2007

Available online 25 May 2007

Abstract

The aim of present Density Functional Theory (DFT) study is the modeling of an activation of molecular oxygen on the manganese porphyrin and a simulation of a set of subsequent processes of hydrogen adsorption, which can lead to the formation of the reactive high-valent manganese-oxo species. Results of the performed calculations reveal that the molecular oxygen may be bound to the reduced manganese porphyrin forming either superoxo or peroxy group. In each case the O₂ molecule is activated. The adsorption of the hydrogen atom on the O₂ molecule leads to the weakening of the O–O bond. The latter is cleaved once the second hydrogen atom becomes adsorbed. As a result the water molecule is formed. The remaining oxygen atom is doubly bound to manganese ion resulting in the high-valent oxo complex.

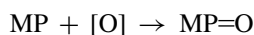
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Keywords: Manganese porphyrin; Dioxygen activation; Homogeneous catalysis; Density functional calculations

1. Introduction

For a number of years metalloporphyrins have been known to catalyze a wide range of oxidation processes in biological systems. As a consequence, they have come under intense studies, especially due to their possible industrial applications as catalysts for selective oxidation of hydrocarbons and their derivatives. Among the variety of metal ions, which have been tested as central atom coordinated by the porphyrin ring, manganese has shown a remarkable catalytic activity in epoxidation and hydroxylation of olefins [1].

The majority of the synthetic porphyrin-catalyzed reactions use O-donors as the oxygen source. As such, the following compounds are usually used: KO₂ [2], PhIO [3], H₂O₂ [4], ClO[−], *m*-chloroperbenzoic acid (*m*-CPBA), HSO₅[−] [5], O₃ [6]. The role of these molecules is to deliver one oxygen atom to the metal active site of the catalyst to form the catalytically active oxo-complex:



Since the side product of the above shown reaction remains in the environment, the current trend in catalytic research is to search for the environment-friendly oxidants. One of the most challenging and promising mediums is the molecular oxygen. Its use is of a great importance for processes of green chemistry and, in addition, molecular oxygen, e.g. as air is a very cheap and abundant oxidant. Numerous catalytic tests have showed that the dioxygen may be effectively used as O-donor in epoxidation of olefins, see e.g. [7–10].

In this case, it is often postulated that the interaction of the molecular oxygen with metalloporphyrins may be similar to the processes known for the P450 cycle that are binding and activation of the molecular oxygen, the subsequent hydrogen adsorption processes, and finally the formation of the reactive oxo complex.

The above-mentioned processes have been already claimed for the manganese-based porphyrin catalyst, however instead of the single hydrogen atom binding subsequent proton and electron addition processes have been postulated [7,11]:



Despite the importance of the problem, the theoretical studies of the dioxygen activation processes on metalloporphyrins are so far limited mostly to the modeling of reactions occurring

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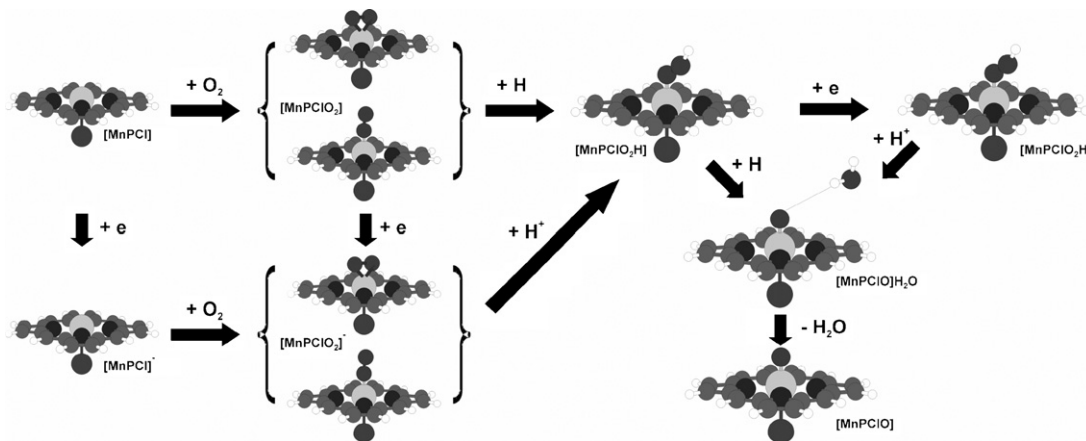


Fig. 1. Investigated processes.

on the active site of the cytochrome P450, which is the iron heme (see e.g. [12–14] and references therein). The published data regarding the geometry and electronic structure of the analogous complexes of manganese(III) are incomplete. Recently, the proposed activation process of the molecular oxygen was studied for the four-coordinate manganese(III) porphyrin using DFT-RPBE method [15]. These studies reveal that the Mn(III) ion preferentially binds dioxygen in the side-on type of complex which, after attachment of one hydrogen atom, may be transformed into the hydroperoxo complex. Once the second hydrogen atom is bound to this species, the oxo-complex is created and a formed water molecule may be released. Moreover, there exist some data on the selected manganese-porphyrin systems. These include the electronic structure of the five-coordinate manganese(II) porphyrin adduct with the O_2 species [16]. Opposite to what is found for the manganese(III) complex, here it is the end-on structure that is more stable than the side-on one. Last but not least, some oxomanganese porphyrin complexes were already the subject of the theoretical studies. The main problem for the theoretical description of the oxomanganese(V) species was to find an appropriate method to reproduce the experimental results concerning the multiplicity of the adduct. Ghosh and Gonzalez [17] investigated three structures, namely $[MnP(PF_6)O]$, $[MnP(Py)O^+]$, and $[MnP(F)O]$, by means of the DFT-PW91/TZP method. The structures were found to be diamagnetic, as proved by the experiment. On the other hand, B3LYP calculations on the $[MnP(H_2O)O^+]$ complex indicated that the diamagnetic complex of Mn(V) lies 0.4 eV higher than the paramagnetic one that may be described as $Mn(IV)P^+ \cdot (H_2O)O^+$ [18]. The same approach applied to $[Mn(\text{corrolato})O]$ complex revealed that this is a closed-shell Mn(V) structure (the higher multiplicities lie higher by 0.1–0.2 eV above the ground state). Other PW91/TZP calculations on this adduct reported the closed-shell Mn(V) state as higher in energy by 0.8 eV than the respective states with higher multiplicities [19]. Recently, two five-coordinate $[MnPO]^+$ systems were described [15,20]. Whereas already-mentioned DFT-RPBE calculations [15] assign the correct spin-state for the oxo complex (singlet as indicated by the experiment), the second one, done with

DFT-UB3LYP/BSI method [20], predicted triplet as a ground state.

The goal of the present research is to mimic the postulated processes of binding and activation of the molecular oxygen by the five-coordinate manganese(III) porphyrin, the subsequent hydrogen adsorption processes, and finally the formation of the reactive manganese(V)oxo complex. The investigated reactions are schematically viewed in Fig. 1.

2. Experimental–theoretical model and method

The above-discussed subsequent reactions are modeled by means of Density Functional Theory (DFT) method using StoBe [21] program code. The choice of the methodology has followed from the fact that it is widely used to study transition metal complexes as well as catalytic reactions of both homogenous and heterogeneous types. The Kohn–Sham orbitals are described by extended all-electron basis sets of the Gauss type orbitals of the DZVP quality [22]. The theoretical model for porphyrin system investigated in this paper consists of $[MnPCI]$ complex, where P denotes porphyrinato ligand, and chlorine ion is considered as a fifth ligand (see Fig. 2). This complex binds O_2 ligand. The geometry optimization of the porphyrin molecule is done with LDA-VWN functional [23]. During all calculations the geometry of the porphyrin ring is frozen assuming that it is not affected by the coordination of the oxygen molecule, by its subsequent decomposition and by the reactions catalyzed by the complex. Therefore, the geometry optimization includes the following atoms: manganese, oxygen, hydrogen, and chlorine.

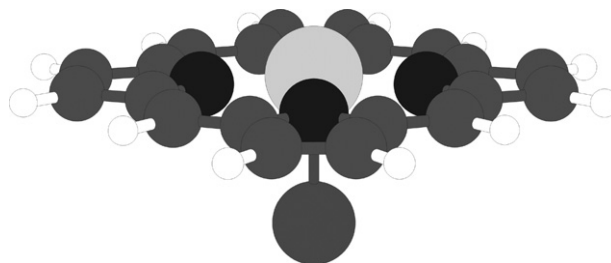
Fig. 2. Model of the investigated $[MnPCI]$ structure.

Table 1
The calculated parameters of the [MnPCl] and [MnPCl][−] systems

Properties		[MnPCl]	[MnPCl] [−]
<i>R</i> [Å]/B.O.	Mn–Cl	2.22/1.23	2.28/0.86
	Mn	0.65	0.79
Charges	Cl	−0.25	−0.50
	P	−0.40	−1.29
	Mn	3.98	4.80
Spin densities	Cl	0.34	0.13
	P	−0.32	0.07

The electronic parameters of the system are then recalculated with GGA-RPBE functional [24,25]. All investigated structures are characterized by atomic charges and spin densities based on Mulliken population analysis [26], Mayer bond indices [27], and binding energies.

3. Results and discussion

In the following, the intermediate structures that are formed during the proposed reactions (see Fig. 1) are described. First, the calculated parameters (gathered in Table 1) of the initial catalyst structure ([MnPCl]) as well as its reduced form ([MnPCl][−]) are discussed.

[MnPCl]. Three multiplicities of the [MnPCl] system are considered, namely 1, 3, and 5. The lowest energy is found for the triplet system, but quintet system is higher only by 0.0002 a.u. in energy. Due to this very small difference in total energy as well as to the fact that quintet is determined as a ground state by experiment [1], state of multiplicity 5 is taken into further consideration. The calculated geometric as well as electronic parameters of the system are collected in Table 1. One can see that the Mn–Cl bond is as long as 2.22 Å and its

bond order equals 1.23. The calculated Mn–Cl bond length is smaller than experimentally measured, which varies between 2.363 and 2.385 Å [28,29], and smaller than determined by Zwaans et al. (2.553 Å) by using HF approach [30]. The discrepancy between the obtained values should be attributed to the fact that LDA often underestimates bond lengths. Four unpaired electrons present in the system are located on the manganese ion.

[MnPCl][−]. For the reduced form of the catalyst, the following multiplicities are considered: 2, 4, and 6. The sextet structure is characterized by the lowest total energy. In the resulting structure the Mn–Cl bond length amounts to 2.28 Å (see Table 1), thus is longer by 0.06 Å than the similar bond in [MnPCl] structure. The bond order of this bond is equal to 0.86 indicating its weakening with respect to not reduced form. The additional electron introduced to the system is located mainly on the porphyrin ring ($\Delta q = -0.89$). The change in charging of the tetrapyrrolic ligand induces the electron transfer from the manganese ion ($\Delta q = 0.14$) towards the chlorine ligand ($\Delta q = -0.25$). Spin density analysis reveals that the unpaired electrons are located on manganese. The energy needed to reduce [MnPCl], calculated as a difference between the two forms, amounts to 194.6 kJ/mol.

As a next step, the possibility of the dioxygen binding by both [MnPCl] and [MnPCl][−] complexes is examined.

[MnPClO₂]. In theory, two geometries for the adsorption of the dioxygen on the metal center should be considered: first, in which the O₂ molecule is bound end-on to the manganese, and the second, where the O₂ molecule is linked side-on to the metal center. For both geometries the calculations are performed for the following multiplicities: 1, 3, and 5. The geometric and electronic parameters of the resulting lowest energy structures (singlet **1** and triplet **2** in Fig. 3, respectively) are listed in Table 2 in the first two columns.

Table 2
The calculated parameters of the investigated dioxygen complexes

Parameter		1 end-on [MnPClO ₂]	2 side-on [MnPClO ₂]	3 end-on [MnPClO ₂] [−]	4 side-on [MnPClO ₂] [−]	Isolated species O ₂ , [MnPCl]
Multiplicities		1	3	2	2	–
<i>E_b^{O₂}</i>		78.2	44.8	−61.9	−23.0	–
<i>R</i> [Å]/B.O.	Mn–O1	1.74/1.10	1.83/0.97	1.73/1.08	1.81/0.99	–/–
	Mn–O2	–/–	1.83/0.97	2.75/0.51	1.92/0.89	–/–
	O1–O2	1.29/1.12	1.31/1.12	1.28/1.22	1.32/1.09	1.22/1.87
	Mn–Cl	2.16/1.27	2.16/1.31	2.24/0.97	2.24/1.04	2.22/1.23
Charges	Mn	0.23	0.24	0.38	0.31	0.65
	O1	−0.07	−0.11	−0.11	−0.17	0.00
	O2	−0.11	−0.11	−0.26	−0.19	0.00
	O ₂	−0.18	−0.22	−0.37	−0.36	0.00
	Cl	−0.11	−0.12	−0.38	−0.34	−0.25
	P	0.06	0.10	−0.63	−0.61	−0.40
Spin densities	Mn	–	1.80	1.41	0.82	3.98
	O1	–	0.21	−0.14	0.25	1.00
	O2	–	0.21	−0.25	0.16	1.00
	O ₂	–	0.42	−0.39	0.41	2.00
	Cl	–	0.02	0.08	−0.02	0.34
	P	–	−0.24	−0.10	−0.20	−0.32

As isolated molecules the [MnPCl] and O₂ species are taken.

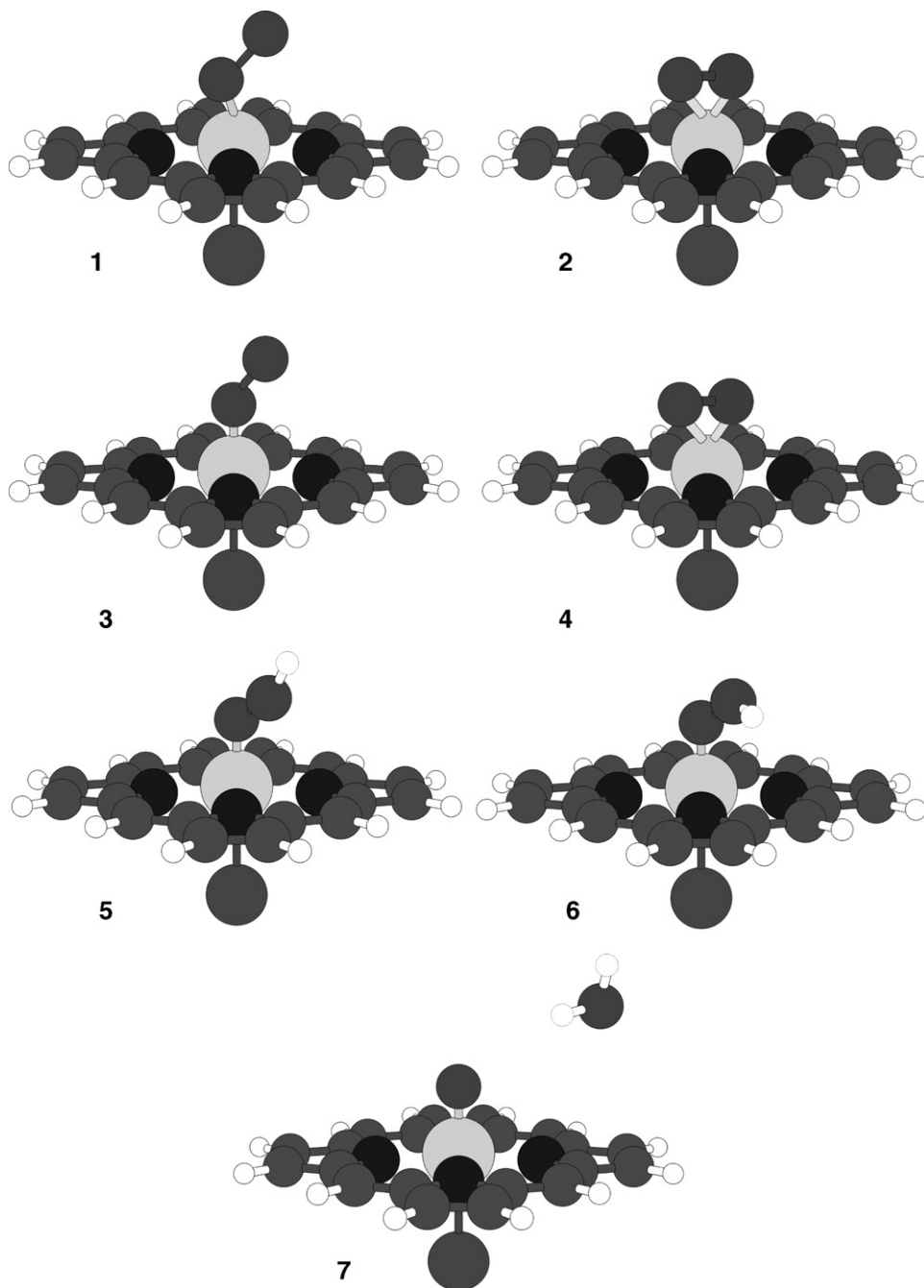


Fig. 3. Investigated structures formed during O_2 binding by $[MnPCl]$ and formation of $[MnPClO]$.

In structure **1** (end-on $[MnPClO_2]$) the molecular oxygen forms with manganese ion the bond of 1.74 Å length and bond order of 1.10 indicating the character of the single bond. The Mn–Cl bond is characterized by length of 2.16 Å and bond order equal to 1.27. Contrary to what might be expected, the longer bond (Mn–Cl) is stronger than the shorter (Mn–O2) one. However one should remember that although the strength of the bond may be indicated by the bond order, which represents the covalent contribution to the bonding between two atoms, the ionic contribution to the bond also counts. Here, the fact that the bond formed by manganese and chlorine is longer than with oxygen

should be attributed to the larger radius of Cl^- in comparison to that of O.

The formation of structure **1** is accompanied by the transfer of 0.46e from the porphyrin moiety to the oxygen molecule ($\Delta q = -0.18$) and to the metal center ($\Delta q = -0.42$). The charge on chlorine ion is changed by 0.14e. The complex is characterized by singlet state. The formation of structure **1** requires 78.2 kJ/mol introduced to the system.

In structure **2** (side-on $[MnPClO_2]$) the distances between both oxygen atoms and the manganese ion are equal to 1.83 Å and the bond orders of both bonds amount to 0.97 suggesting

that the two oxygen atoms are equivalent and singly bonded to the manganese ion. The fact that both Mn–O are equidistant is with agreement with X-ray structures of both known side-on manganese(III) complexes [31,32]. The mode of the coordination of the oxygen molecule has only a small influence on the Mn–Cl bond. In this structure its length is equal to 2.16 Å and bond order to 1.31. The comparison of the strength of the studied bonds in structure **2** reveals that here the Mn–Cl bond is more covalent than any of the single Mn–O bond. However, one should have in mind that both oxygen atoms are equally participating in the bonding between the oxygen molecule and the manganese ion. Therefore, the O₂ molecule is stronger bound to Mn than Cl[−] ligand. Coordination of the oxygen species in this manner results in the shift of 0.50e from the porphyrin ligand and electrons are divided between the Mn ($\Delta q = -0.41$) and O₂ ($\Delta q = -0.22$) moieties. Chlorine ion changes its charge by 0.13e. The resulting system is paramagnetic with two unpaired electrons located on the manganese ion and partially on the oxygen atoms antiparamagnetically coupled with the negative spin density on the porphyrin ring. The binding of dioxygen to form the structure **2** costs 44.8 kJ/mol.

The analysis of the parameters characterizing end-on (**1**) and side-on (**2**) structures shows that in both cases the bonding of the O₂ molecule into manganese porphyrin results in the activation of O₂ species. This is expressed by the elongation of the O–O bond from 1.22 Å in the free isolated O₂ molecule to 1.29 Å in structure **1** and to 1.31 Å in structure **2**. The latter bond length is smaller by 0.11 Å in comparison to its value given by experiment [32]. Simultaneously, the O–O bond order diminishes from 1.87 (gaseous oxygen) to 1.12 in both **1** and **2** species. The elongation and weakening of this bond is accompanied also by enrichment in electron density of the O₂ molecules. This results in the negative charging of the bound O₂ molecule. In end-on (**1**) case the negative charge is located mainly on the outer oxygen atom from the O₂ ligand. This has impact on the reactivity of the Mn–O₂ group, because the negative charge of the oxygen atom is one of the factors facilitating the electrophillic attack of protons. Moreover, due to the lack of steric hindrance the electrophillic attack should be even easier on the outer oxygen. In side-on structure **2** the excess charge is equally distributed between the two oxygen atoms. Taking into account elongation of O–O bond and charging of O₂ ligand one may conclude that the side-on mode of coordination of the O₂ species causes slightly larger activation of the latter. The observed changes in the region of the O₂ group facilitate all processes requiring the cleavage of this bond including the oxidation of organic molecules.

The common point in the formation of both **1** and **2** structures is that the porphyrin ring acts as the main reductor in the studied processes. The structure in which the oxygen molecule is bound side-on (**2**) has lower total energy than the one where it is bound end-on (**1**); the difference in total energies between the two structures is equal to 45.2 kJ/mol. This indicates structure **2** as the predominant in real systems.

[MnPClO₂][−]. For the reduced system similarly as for [MnPClO₂], two starting geometries are considered: end-on and side-on, and two multiplicities are taken into account.

In structure **3** (end-on [MnPClO₂][−]) the dioxygen species forms with the manganese ion a bond of 1.73 Å, which bond order amounts to 1.08. These parameters indicate a single bond. The length of axial bond to chlorine ligand is 2.24 Å with bond order equal to 0.97. It should be noted here, that the similar bond in the reduced form of the catalyst ([MnPCl][−]) amounts to 2.28 Å with the bond order equal to 0.50. Thus, one can conclude that the Mn–Cl bond is strengthening as a result of the coordination of the dioxygen moiety. Taking into account the bond order of the manganese–axial ligand bond it is seen that the two ligands form the bonds of comparable covalence.

The considerations of the electron transfer accompanying formation of structure **3** from O₂ and [MnPCl][−] (compare Table 1) may be described as follows. There are 0.37e transferred onto the O₂ moiety. These are located mainly on the outer oxygen, the oxygen that is connected to the metal ion is less charged. The manganese ion is reduced, whereas the porphyrinato and chlorine ligands are mildly oxidized. When comparing with not reduced complex [MnPClO₂] one sees that the additional electron goes mainly to P ring. Some portion accumulates also on Cl[−] and oxygen moiety. Reduction process involves only ligands; the manganese ion undergoes slight oxidation.

In the resulting structure spin density on the manganese ion equals 1.41 and on the dioxygen ligand to −0.39 showing the antiferromagnetically coupling of electrons. Spin densities on the porphyrinato and chlorine ligands have smaller values.

The O₂ species is spontaneously stabilized on the reduced [MnPCl][−] complex, the binding energy equals to −61.9 kJ/mol.

In structure **4** (side-on [MnPClO₂][−]) the two Mn–O bonds are not equivalent. Their lengths amount to 1.81 Å and 1.92 Å and bond orders are equal to 0.99 and 0.89, respectively. The Mn–Cl bond is of the same length as in already discussed end-on complex and its bond order amounts to 1.04, that is by 0.07 more than in species **3**. The comparison of the Mn–Cl bond parameters in system **4** and [MnPCl][−] reveals that the coordination of the molecular oxygen results in its shortening by 0.04 Å and, what follows, its strengthening expressed by the increase of the bond order by 0.54.

The formation of this dioxygen adduct from O₂ and [MnPCl][−] is accompanied by the oxidation of the porphyrin ligand and the reduction of the central atom. A significant (amounting to 0.36e) electron transfer towards the O₂ molecule is found. In the resulting structure the two oxygen atoms are almost identically charged. The chlorine ion loses a part of its negative charge. When comparing structure **4** with not reduced system **2** one notices that the additional electron is redistributed mainly on P ring ($\Delta q = -0.71$) and trans ligand Cl[−] ($\Delta q = -0.22$). About 0.18e goes onto O₂ species and metal undergoes slight oxidation ($\Delta q = 0.07$).

In complex **4** the unpaired electron is located mainly on the central atom (spin density 0.82) and on the dioxygen ligand (spin density 0.41). These are antiferromagnetically coupled with 0.20 located on the porphyrin moiety.

The dioxygen binding to the reduced catalyst that results in structure **4** is an exoenergetic process. The calculated energy needed for this process amounts to −23.0 kJ/mol.

Similar as in structures **1** and **2**, the bound O₂ species is also activated in systems **3** and **4**. This is seen by the elongation and weakening of the O–O bond in both structures as well as by the already discussed electron transfer to the O₂ fragments. In system **3** the O–O bond length amounts to 1.28 Å and is longer by 0.06 Å than in isolated O₂. Its bond order is lowered by 0.65 and in the resulting structure equals 1.22. The changes in the structure of the O–O bond are even larger in species **4**. Here, the O–O bond is as long as 1.32 Å with bond order of 1.09. As compared to the free molecular oxygen, it is elongated by 0.10 Å and weakened by 0.78 (as a measure of the weakening, the change in bond order is taken). Overall, the oxygen molecule is more activated while bound side-on than end-on to the reduced catalyst.

Structure **3**, in which the O₂ species is bound end-on, is characterized by lower total energy than structure **4**. In both cases the process is thermodynamically exothermic. The energy difference amounts to 38.9 kJ/mol. This indicates the former structure as a predominant in the real system. This is opposite to what is found for structures **1** and **2**, where the dioxygen prefers the side-on mode of coordination and addition of O₂ ligand requires the energy (endothermic reaction).

To sum up this part of our studies, it should be pointed out that the binding of the O₂ ligand is thermodynamically privileged to the reduced form of the catalyst ([MnPCl][−]) than to the starting form of the catalyst ([MnPCl]). This finding indicates that in the reaction conditions the system would tend to reduce before the dioxygen-binding step. This suggestion seems to be supported by the observation of the dioxygen binding process in electrochemical experiment [7,11]. The form of the resulting dioxygen adduct would be the end-on structure in which the O₂ ligand is strongly activated. This is seen not only by the elongation and weakening of the O–O bond, but also by the large electron transfer towards dioxygen moiety. These findings have serious implications regarding catalysis, since the above-described changes in the region of the O–O bond would facilitate its rupture and insertion of one of the oxygen atoms to the substrate molecule during the oxidation reaction catalyzed by this complex. Further, the accumulation of the negative charge on the dioxygen species generates a new nucleophilic region in the studied catalyst strongly influencing its activity. It should be mentioned here, that the additional charge is not distributed homogeneously. The outer oxygen atom, which suffers less from steric hindrances than the one connected to the central atom, is more negatively charged than the other what, taking into account that this is the one that reacts with a substrate, affects strongly the reactivity of the complex. One may thus conclude that 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.

[MnPClO₂H]. As a next step, the interaction of hydrogen atom with the molecular oxygen bound to the porphyrin complex ([MnPClO₂]) is discussed, that may be considered either as the situation in which the atomic hydrogen is abstracted from an organic molecule staying in proximity to the catalyst or as the interaction of proton with the reduced [MnPClO₂][−] complex.

Table 3
The calculated parameters of the investigated systems **5** and **6**

Parameter	[MnPClO ₂ H] (5)	[MnPClO ₂ H] [−] (6)	
E_b^{OH}	−115.9	−	
$E_b^{\text{O}_2\text{H}}$	−130.1	−	
R [Å]/B.O.	Mn–O1	1.82/0.95	1.60/1.72
	O1–O2	1.40/0.95	1.75/0.55
	O–H (O ₂ H)	0.99/0.77	0.99/0.82
	Mn–Cl	2.19/1.23	2.28/0.92
Charges	Mn	0.42	0.41
	O1	−0.26	−0.26
	O2	−0.36	−0.57
	O–H (O ₂ H)	0.07	−0.20
	O–O–H (O ₂ H)	−0.19	−0.46
	Cl	−0.18	−0.41
	P	−0.05	−0.54
Spin densities	Mn	3.19	−
	O1	0.06	−
	O–O–H (O ₂ H)	0.07	−
	Cl	0.15	−
	P	−0.42	−

Hydrogen becomes stabilized on oxygen independent of way in which dioxygen binds to manganese (structure **5**, see Table 3 and Fig. 3) forming so-called hydroperoxo group (OOH). Three multiplicities (2,4,6) are considered for the [MnPClO₂H] complex. The resulting complex possesses three unpaired electrons, located mainly on the metal center.

Delivery of the hydrogen atom leads to further elongation and weakening of the O–O bond. The O–O distance increases to 1.40 Å and the bond order decreases to 0.95. Now, only one oxygen atom is attached to manganese ion. The Mn–O bond is characterized as a single bond of the length of 1.82 Å. The parameters of this bond do not differ much from the ones obtained for the bond between the manganese ion and the closer oxygen atom (in Table 2 denoted as O1) while compared with structure **2**. On the other hand, the Mn–O bond length is increased as compared to structure **1** and, what follows, the bond order is diminished. The second oxygen atom is forming a single bond with the hydrogen atom. The length of this bond is equal to 0.99 Å.

As can be seen from Table 3, the Mn–Cl bond is a little affected by hydrogen adsorption on the [MnPClO₂] structures; its length increased by 0.03 Å as compared to these values in structures **1** and **2**, and bond order decreased to 1.23. On the contrary, larger changes are observed when the parameters of the Mn–Cl bond are compared with the analogous bond in the reduced [MnPClO₂][−] complexes. This is decreased by 0.05 Å as compared to appropriate values in **3** and **4** structures. Consequently, this bond order is augmented by 0.23 and 0.19, respectively.

The adsorption of the H atom results in the oxidation of the Mn ion—its charge increases by 0.19–0.18 as compared to structures **1** and **2**, respectively. The charge on both O1 and O2 is diminished. For O1 it is lowered by 0.19 and 0.15 for complexes **1** and **2**, respectively, whereas for O2 it is less by 0.25 as compared to the O2 charge in both **1** and **2** species. However,

taking into account the fact that the incoming hydrogen atom is positively charged the total charge on this axial ligand of O–O–H type ($q_{O_2H} = -0.19$) is changed insignificantly (it amounts to -0.18 in **1** and -0.22 in **2** structures). The porphyrin ring accepts 0.11e and 0.15e as compared to structures **1** and **2**, respectively. In the resulting structure the OH type fragment (O₂H) is slightly positively charged.

One can guide the discussion also as adding H⁺ onto the reduced [MnPClO₂][−] complex (structure **3**). Then, the adsorption of proton is accompanied by the oxidation of the porphyrin and chlorine ligands. The difference in charges on both manganese ion and the second axial ligand is negligible.

The situation is somewhat different when the discussion is lead as adding H⁺ onto the reduced complex [MnPClO₂][−] where O₂ is side-on bonded (structure **4**). In such a case the major changes in charging of the complex fragments is found for porphyrin and chlorine ligands ($\Delta q = 0.56$ and 0.18, respectively), the changes on the remaining fragments amount to 0.11 and 0.17 for Mn and O₂H, respectively.

One can calculate the binding energy of different fragments. The OH binds to [MnPClO] with energy of -115.9 kJ/mol, whereas O–O–H species (O₂H) to [MnPCl] with energy that amounts to -130.1 kJ/mol.

It should be mentioned here that the formed hydroperoxo complex is often postulated as possessing catalytic significance. This species may be the source of either OH or OOH fragments during oxidation of hydrocarbons catalyzed by metalloporphyrins [1]. In this respect, the theoretical description of the complex is of the utmost importance. The performed studies reveal that the formation of this species is possible and the analysis of the geometric and electronic parameters suggests that the hydroperoxo complex may be catalytically active. First of all, the further activation of molecular oxygen supports this statement. As was already invoked, the longer and weaker the bond, the easier to split it and transfer the formed groups to the reactant. Secondly, it is worth to mention that in this complex both oxygen atoms, O1 and O2, are highly negatively charged. This observation may somehow explain the postulated reactivity of the studied adduct, because these are the atoms that attack the organic molecule in the course of catalytic reaction (O1 if the whole OOH group, or O2 if only a OH fragment, are transferred). Finally, although OOH and OH fragments are strongly bound to the catalyst, their delivery to the organic molecule may be feasible. This would be a case if the energies reported in the present paper were corrected to contain the binding energy of the transferred fragment (OOH or OH) to the reactant.

[MnPClO₂H][−]. The parameters of this complex, referred to as structure **6**, are listed in Table 3. For this system three multiplicities, namely 1, 3, and 5, are taken into consideration. The comparison of the total energies of the investigated structures indicates that the singlet state is characterized by the lowest total energy.

The reduction of the [MnPClO₂] complex (structure **5**) and formation of [MnPClO₂H][−] (structure **6**) is accompanied by the significant elongation of the O–O bond from 1.40 Å in **5** to 1.75 Å in **6** as well as by the elongation of the Mn–Cl bond from 2.19 Å in **5** to 2.28 Å in **6**. As a result both bonds become

Table 4

The comparison of the calculated parameters for structure **7** and the isolated [MnPClO] complex

Parameter		[MnPClO] + H ₂ O (7)	[MnPClO]
<i>R</i> [Å]/B.O.	Mn–O	1.56/2.07	1.54/2.22
	Mn–Cl	2.20/1.22	2.20/1.20
Charges	Mn	0.25	0.28
	O	−0.26	−0.17
	Cl	−0.18	−0.16
	P	0.05	0.05

weakened. The O–O bond order is equal to 0.55. Thus, the bond is very weak. Additionally, the parameters of the Mn–O bond indicate that the bond character is better described as a double bond. Its length amounts to 1.60 Å, whereas the bond order is equal to 1.72. All in all, structure **6** represents the system in which the O–O bond is about to break and the oxo group is almost formed.

The O–H (O₂–H) bond length is the same (0.99 Å) and bond order equals 0.82 against 0.77 in complex **5**.

The additional electron introduced to non-reduced structure **5** is located mainly on the porphyrin moiety ($\Delta q = -0.49$) and to a lesser extend on the O₂H and Cl[−] ligands ($\Delta q = -0.27$ and -0.23 , respectively). Interestingly, as far as the O–O–H (O₂H) fragment is concerned, the changes in charging of O2 and H atoms are responsible for the observed effect (these are $\Delta q = -0.21$ and -0.07). The atomic charge on O1 is constant. The charge changes on the central atom amount to 0.01.

[MnPClO]H₂O. This structure results from adding the second hydrogen atom to [MnPClO₂H] complex or adding a proton to the reduced [MnPClO₂H][−] system. Three multiplicities of the [MnPClO]H₂O structure are calculated, singlet, triplet, and quintet and the singlet complex is found as characterized by the lowest total energy.

Delivery of the second hydrogen atom to **5** or the second proton to **6** promotes the cleavage of the O–O bond and results in the formation of the H₂O molecule, which may desorb, leaving the oxo group on the porphyrin complex (see Fig. 3 structure **7**, and Table 4). In the resulting complex ([MnPClO]) the Mn–O bond is considerably shortened and strengthened as compared to the similar bond in previously described structures. Here, the Mn–O distance is equal to 1.56 Å and this bond order is equal to 2.07 indicating the double character of the Mn–O bond. The bond between the manganese and chlorine ions becomes slightly weaker and longer than in **1**, **2**, and **5** complexes illustrating the mutual dependence between all bonds formed by the metallic center with axial ligands; the strengthening of one bond causes the weakening of the other. On the other hand, as compared to the negatively charged structure **6**, this bond length is shortened by 0.04 Å and this bond order is increased by 0.26.

The H₂O molecule formed in this reaction is weakly bonded to the oxo group of the catalyst. Water binding energy in the investigated complex is calculated to be 1.3 kJ/mol. The distance between one of the hydrogen atoms from H₂O moiety and the oxygen atom from the oxo group amounts to 1.88 Å. As a con-

sequence, the larger polarization of the O=Mn–Cl group than in the isolated [MnPClO] complex is observed. This is expressed by the shift of the negative charge towards the oxygen atom in the resulting complex (the charge on the oxygen atom from the oxo group in **7** is equal to -0.26 against -0.17 in the isolated [MnPClO] complex (for comparison see Table 4)). The Mn–O bond is longer by 0.02 \AA and its bond order is lower by 0.15 than in the isolated [MnPClO] molecule. While the Mn–O distance in isolated MnPClO amounts to 1.54 \AA , the same bond in the similar complex, [MnPFO], calculated within DFT-PW91/TZP approach is reported to be as long as 1.561 \AA [17]. The changes in the parameters of the Mn–O bond do not affect the parameters of the Mn–Cl bond.

Our theoretical studies seem to prove that the reactive oxo species may be formed in the proposed way. As already mentioned, this form of catalyst is postulated to be of great catalytic activity [1]. The resulting complex possesses a new, highly nucleophilic center, which is the oxo group. This group may abstract protons (or hydrogen atoms) from the reactants as well as may be transferred to the organic species as happens. Although the reported theoretical parameters of the Mn–O bond show it is short and strong in terms of thermodynamics, the experimental data indicate that the reactivity of this bond should be attributed to its labile character and not to oxygen binding energy.

4. Conclusions

In summary, the results of the DFT calculations show that the molecular oxygen may be bound to the manganese porphyrin forming either side-on or end-on group. The dioxygen binding occurs after the reduction of the catalyst. This is indicated by dioxygen binding energies, positive (endothermic process) in case of binding to the non-reduced [MnPCI] complex (equal to 78.2 kJ/mol and 44.8 kJ/mol for end-on structure **1** and side-on structure **2**, respectively), and negative (exothermic process) in case of binding to the previously reduced [MnPCI][−] complex (equal to -61.9 kJ/mol for end-on structure **3** and -23.0 kJ/mol for side-on structure **4**). No matter the geometry of the bound dioxygen ligand is, the O₂ species is activated in such a way that the processes requiring the cleavage of the O–O bond are facilitated. The adsorption of the single hydrogen atom or proton leads to the further elongation and weakening of the O–O bond, whereas the adsorption of the second hydrogen atom or proton induces the cleavage of this bond. The water molecule is formed and the remaining oxygen atom on the porphyrin complex is forming the oxo group. This complex is known as possessing the catalytic activity.

Last but not least, our studies reveal that the manganese porphyrin is a very versatile system of a great catalytic importance. This is due to the fact that after dioxygen binding it may exist in a variety of forms (side-on and end-on adducts with dioxygen,

hydroperoxo and oxo) whose parameters indicate high-catalytic reactivity.

Acknowledgement

The authors acknowledge the use of facilities at the Academic Supercomputer Center CYFRONET grant no. KBN/SGI2800/PAN/019/2001.

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