Quantum Chemical Description of Oxygen Activation Process on Co, Mn, and Mo Porphyrins[†]

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Abstract: The aim of the present theoretical study is to examine the dioxygen activation process occurring at the metalloporphyrin complexes as the first step of the selective oxidation of hydrocarbons, with the stress put on how this may be affected by the type of the central metal. In order to do so, the properties of the porphyrin complexes of Mn, Mo, and Co are discussed by means of quantum chemical calculations within Density Functional Theory (DFT). As a first step, the dioxygen binding by the above-mentioned systems is considered, followed by the study of the interactions of one and two hydrogen atoms with different types of the adsorbed O_2 molecule onto the porphyrin complex. Finally, the stability of the formed oxo species is discussed.

1. Introduction

Molecular oxygen is a stable paramagnetic molecule with two unpaired electrons; therefore, its reactions with organic substrates, that are usually diamagnetic, are spin-forbidden. Consequently, there is an interest to activate dioxygen so that the oxidation reaction is possible. Among numerous possibilities, the activation of the molecular oxygen may be caused by bonding it to the appropriate center, which usually is a transition-metal atom, e.g., in a coordination compound. Within the last years one of the most popular complexes used to activate the dioxygen molecule became metalloporphyrins. In this class of compounds, a metal ion is equatorially coordinated by the porphyrinato ligand, which may be substituted by different groups (see Figure 1).

The interest in metalloporphyrins is due to the presence of their analogues in different proteins where they serve as dioxygen binding sites as well as active centers of numerous enzymes responsible for bio-oxidation. Their ability to maintain oxidation of organic molecules is the origin of metalloporphyrin-based catalysts for hydrocarbons oxidation in mild conditions.[1] One of the most important advantages of the metalloporphyrins is the possibility of changing their geometric and, at the same time, electronic structure in order
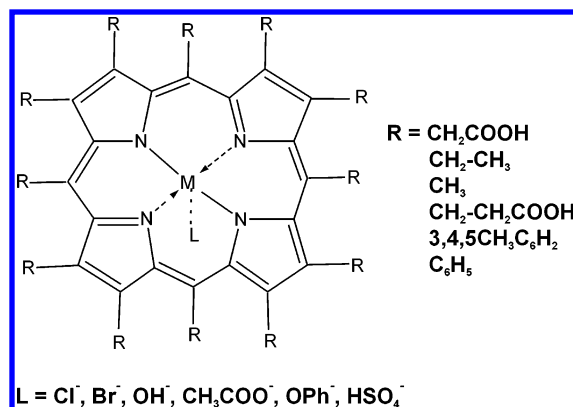

Figure 1. The geometric structure of metalloporphyrins.

R = CH₂COOH, CH₂-CH₃, CH₃, CH₂-CH₂COOH, 3,4,5CH₃C₆H₂, C₆H₅

L = Cl⁻, Br⁻, OH⁻, CH₃COO⁻, OPh⁻, HSO₄⁻

to tune their catalytic properties. This is usually done by modulating the character of the porphyrinato ligand substituents (from electron-donating to electron-withdrawing), by changing the central metal ion (its type and oxidation state), or, finally, by modifying the axial ligand that is bound in the trans position with respect to the dioxygen binding site. Such a dependence may be rationalized in the following way. The catalytic oxidation by porphyrins with dioxygen comprises binding of the O_2 molecule to the metal center. The metal-bound dioxygen species may form different geometric structures (side-on and end-on) and may be transformed into other reactive species (hydroperoxo and oxo)—see Figure 2. The possibility of the existence of different forms of so-
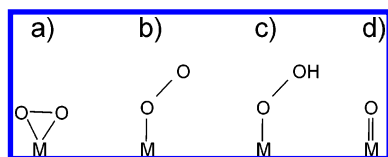
Figure 2. Selected catalytically active forms of oxygen: (a) side-on, (b) end-on, (c) hydroperoxo, and (d) oxo.

Figure 3. Model of the porphyrin molecule.

called "active oxygen species" as well as their electronic properties and, what follows, their reactivity depend on the character of bonding defined by the type of the central metal as well as on the type of the surrounding ligands. That is why the influence of the metal center on the dioxygen binding appears to be of primary importance.

In order to study the influence of the metal type on the dioxygen activation process the porphyrin complexes of Mn, Co, and Mo are chosen. The selection of these metals results from the fact that their compounds fall into three distinct classes while regarding their catalytic behavior.

On the one hand, the manganese porphyrins are known as moieties that mimic the processes known for the cytochrome P450, which is the cycle of binding and activation of the molecular oxygen, the subsequent process being hydrogen adsorption, and finally the formation of the reactive oxo-complex. The above-mentioned processes are postulated for the manganese-based porphyrin catalysts based on electrochemical experiments; however, instead of the single hydrogen atom binding subsequent proton and electron addition processes were postulated:[2]

$$Mn(III) + O_2 + 2e + 2H^+ \rightarrow Mn(V)O + H_2O$$
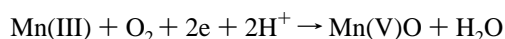
Consequently, a variety of different forms (dioxygen, hydroperoxo, and oxo complexes) may be formed. As catalysts, they are very active in epoxidation and hydroxylation of hydrocarbons under mild conditions.[1]

On the other hand, the experimental evidence suggests that the cobalt porphyrins do not form the oxo species, and thus their catalytic activity is attributed mainly to the dioxygen-bound forms of these complexes as well as to their hydroperoxo derivatives.[1] The dioxygen derivatives of these compounds are formed during the catalytic oxidation of hydrocarbons with dioxygen as the oxidant, whereas the presence of hydroperoxo forms of cobalt porphyrins is claimed during the oxidation reactions with either hydrogen peroxide (H_2O_2) or hydroperoxides (ROOH) as oxidants. Similarly to the manganese porphyrins, the cobalt porphyrins are successfully applied for oxidation of hydrocarbons.[1]

Finally, the molybdenum porphyrins are known due to their catalytic and photochemical behavior.[3] The experimental evidence clearly indicates that molybdenum may coordinate all considered "reactive oxygen species" (i.e., dioxygen, hydroperoxide ligand, and oxo group).[1,4,5] In addition, in the coordination compounds, the molybdenum ions are known as being able to form multiple oxygen groups.[7] The molybdenum complexes are used as stereoselective catalysts for epoxidation of olefins,[7,8] but the nature of oxidizing species is not clearly established. In particular, the requirement of the olefin activation through its coordination to the

metal center prior to the oxygen transfer step is still a matter of controversy.

Up to our knowledge, the theoretical studies of the dioxygen activation processes on metalloporphyrins are limited mostly to the modeling of reactions occurring on the iron porphyrin, especially on the iron heme (see e.g., refs 9 and 10 and references therein). This is due to the fact that this process is observed in the cytochrome P450, as mentioned above, and is of great physiological importance. The similar studies for manganese, cobalt, and molybdenum porphyrins are not known. Regarding the geometry and electronic structure of the complexes which may be formed during this process, very little data have been published so far. The literature provides one with the theoretical study of the six-coordinate dioxygen complex of cobalt porphyrin with imidazole as the axial ligand.[11] According to this study, the oxygen molecule is bound end-on to the metal center. Moreover, the electronic structure of the five-coordinate manganese porphyrin adduct with the O_2 species is also known,[12] but the studies were performed for manganese(II) and not for manganese(III) as in the present study. For that complex, the end-on structure is more stable than the side-on one. Finally, selected examples of the oxomanganese poprhyrin complexes were already the subject of the theoretical studies. Most of them consider the six-coordinate complexes.[13–15] Very recently, the five-coordinate [MnPO]$^+$ system has been characterized with the DFT-UB3LYP/BSI method,[16] but its spin state (triplet) was not correctly predicted as compared with the experiment (singlet).

Taking into account all data published so far, our study would be the first not only to model the process of dioxygen activation via subsequent two hydrogen atoms adsorption but also to present the structure and properties of the formed five-coordinate Mn, Co, and Mo porphyrin complexes with the studied ligands.

Therefore, the interest of the present studies is focused on the behavior of Mn, Co, and Mo compounds in dioxygen binding and activation processes in order to examine which parameters of the metal ions are responsible for their catalytic activity. Moreover, the aim is to check the ability of the studied porphyrins to activate the molecular oxygen via hydrogen binding.

2. Methods

Model. As a geometrical model taken into theoretical simulations, the MP complex (where M = Co, Mn, Mo, and P = porphyrinato ligand) is chosen where all peripheral substituents of the macrocyclic ring are replaced by hydrogen atoms (see Figure 3). Such a choice assures that the examined effect is purely due to the chemical character of the central metal ion, which is chosen on its typical (for coordination compounds) formal valence state, i.e., Co^{2+}, Mn^{3+}, Mo^{4+}. As a result, the studied MP complex is differently charged

Table 1. Electronic Parameters (Charges *Q* and Sum of Bond Orders) of the Initial MP Complexes (M = Co, Mn, Mo)

MP	CoP MULT 2	MnP MULT 5	MoP MULT 5
Q(M)	0.56	1.00	1.23
bond orders ΣM−N	2.72	2.64	2.40

depending on the system, and total charges are equal to 0, 1, and 2 for CoP, MnP, and MoP, respectively.

Computational Method. The calculations are performed by means of ab initio quantum chemical Density Functional Theory method within GGA-RPBE functional,[17,18] as implemented in StoBe computer code.[19] In this approach, the Kohn−Sham orbitals are described by extended all-electron basis sets of contracted Gaussians.[20] All electron basis sets of DZVP quality are applied for all atoms, except for Mo atom, where the model core potential is used.[21]

The energy self-consistency convergence criteria is 10^{-6} au, whereas the energy gradient convergence for the geometry optimization is 10^{-4} au.

The studied systems are discussed in terms of electronic (Mayer bond indices,[22] Mulliken charges[23]) and geometric (bond lengths, and valence angles) parameters. In addition, each system is characterized by binding energies of the studied oxygen species.

Since the preliminary calculations show that the relaxation of the porphyrin ring is negligible upon binding of a small ligand O_2 (maximum displacement of atoms is ca. 0.03 Å), in the present calculations the optimization comprises only the metal ion and the adsorbed species.

In each case the calculations are performed for different spin states, which are possible for a given system to occur. Nevertheless, in this paper it is decided to include only the results for the systems of the multiplicities that are characterized by the lowest total energies.

3. Results and Discussion

The discussion of the results is organized as follows. First, the calculations of the four-coordinate porphyrin complexes of Co, Mn, and Mo are presented. Second, the dioxygen binding process by the above-mentioned systems is considered. The analysis of the O_2 binding energies allowed one to define the preference of each of the metalloporphyrins to form either end-on or side-on structures. Next, the interaction of the atomic hydrogen with the O_2 molecule bound to the porphyrin complex is taken into account and followed by the investigations of the bonding of second hydrogen atom leading to the formation of the hydroperoxo and oxo species, respectively. Finally, the properties of the different (Co=O, Mn=O, Mo=O) oxo species are discussed.

The Four-Coordinate MP Complexes. Table 1 collects electronic parameters of all studied four-coordinate MP complexes. The ground-state of both MnP and MoP complexes is found to be high-spin (multiplicity equal to 5), whereas the CoP complex is low-spin (multiplicity equal to 2).

In the studied complexes the metal ions always lie in the plane of the macrocyclic ligand. The interesting point,

Table 2. Binding Energies of the O_2 Molecule at the MP Complexes (M = Co, Mn, Mo)

$E_B(O_2)$ [eV]	CoP	MnP	MoP
side-on	1.56	−0.08	−2.55
end-on	−0.28	0.30	−1.84

however, is that in the case of the lower-spin molybdenum systems, the Mo position is significantly out of plane. The displacement of the Mo ion is calculated to be 0.49 Å and 0.28 Å for the systems of multiplicities equal to 1 and 3, respectively.

The bond order indices show that the covalent character of metal−nitrogen bond slightly changes in order Co−N > Mn−N > Mo−N, nevertheless the differences are almost negligible (the largest is 0.08 per M−N bond).

In agreement with chemical intuition, in the studied four-coordinate complexes the charge on the metal sites scales with their formal valence state (Co^{2+}, Mn^{3+}, Mo^{4+}). The Co ion exposes the smallest positive charge (+0.56), larger quantifies the Mn atom (+1.00), whereas the largest (+1.23) charge characterizes the Mo site. Since the charge accumulated on the central metal may be the measure of the electrophilicity of an active center of a catalyst, the performed calculations suggest that the cobalt porphyrin would be characterized by the least electrophilic center, while molybdenum porphyrin would possess the most electrophilic one among the studied complexes.

Dioxygen Binding. As mentioned before, dioxygen may be bound to the metal center forming either end-on or side-on complexes. In order to investigate the structure of metal−dioxygen bond in the studied compounds the geometry optimization is performed taking as a starting point two distinct geometries: side-on and end-on. The possibility of the existence of each of these structures and, further, its stability may be deduced form the binding energy of the O_2 molecule to the MP complex. This is calculated as a difference between the total energy of the MP−O_2 complex and a sum of the total energies of the MP and O_2 fragments:

$$E_B(O_2) = E(MP-O_2) - [E(MP) + E(O_2)]$$

Table 2 summarizes the binding energies and clearly shows the differences among the studied systems. The cobalt porphyrin would only form the end-on type complex; the negative dioxygen binding energy indicates the thermodynamically stable bond. The formation of the thermodynamically unstable, side-on form of the $CoPO_2$ system would cost as much as 1.56 eV. The manganese porphyrin, in contrast, would bind dioxygen exclusively in the side-on type of geometry. These predictions are in line with the experimental evidence for the end-on $CoPO_2$ and side-on $MnPO_2$ geometries.[24,25] It is worth mentioning that the formation of the end-on form of the manganese complex (thermodynamically unstable) would be less energetically demanding ($E_B(O_2)$ = 0.30 eV) than the formation of the side-on derivative of the cobalt porphyrin (neither thermodynamically stable, $E_B(O_2)$ = 1.56 eV). Finally, the negative binding energies of O_2 in the side-on and end-on complexes of the molybdenum porphyrin indicate that both these forms of the Mo−O_2 group

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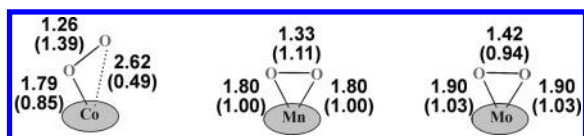

Figure 4. Bond lengths in [Å] and Mayer bond orders indices (in parentheses) for the bound O_2 molecule at the MP system (M = Co, Mn, Mo).

may exist; however, the formation of the side-on complex is favored by 0.71 eV over the end-on form.

The comparison of the resulting energies of the $M-O_2$ bonds indicates that the bond with the manganese ion is the weakest among the studied metal-dioxygen ones. The molybdenum porphyrin, irrespective of the geometry of the $M-O_2$ group, binds dioxygen the strongest.

In the following, only the systems characterized by the lowest total energies will be characterized. These are end-on $CoP-O_2$, side-on $MnP-O_2$, and side-on $MoP-O_2$ whose parameters (bond lengths and bond order indices) of the newly formed bonds are presented in Figure 4.

The analysis of the resulting dioxygen complexes reveals that only in the case of the molybdenum porphyrin the binding of the O_2 molecule results in a movement of the Mo ion up out of plane (the Mo displacement is ca. 0.50 Å). The in-plane positions of both, manganese and cobalt ions, are intact upon the dioxygen binding. In each studied complex the O_2 binding leads to the formation of the single metal$-$oxygen bonds (with bond lengths ca. 1.80 Å), what may be also seen from the $M-O$ bond order (ca. 1.00). In case of both side-on complexes, one notices that the $M-O$ bonds are symmetric, i.e., both have the same length and strength (see Figure 4).

In all cases, the binding of the O_2 molecule to the investigated metalloporphyrins results in the elongation of the $O-O$ bonds (1.22 Å in the isolated molecule). The effect, relatively small for the cobalt porphyrin (elongation by 0.04 Å), is more pronounced in the side-on Mn and Mo complexes, where the bond lengths expand by 0.11 Å and 0.20 Å, respectively. Together with the elongation of the $O-O$ bonds, their weakening is observed, which is reflected by the decrease of the respective bond orders as compared to the isolated O_2 molecule (B.O. = 1.87). These are in line with the trend observed for the elongation of the $O-O$ bonds in the studied compounds; the weakening of this bond is the smallest (ΔB.O. = 0.48) in the cobalt porphyrin, larger in the manganese complex (ΔB.O. = 0.76), and the largest in the molybdenum porphyrin (ΔB.O. = 0.93).

The O_2 binding leads to the rearrangements of the electrons in the studied complexes, which may be quantified by the changes of the charges accumulated on the fragments of the molecules. Table 3 collects the Mulliken charges of the metal and the adsorbed oxygen atoms of the $MP-O_2$ complexes. The analysis of the charge redistribution after the dioxygen binding allows for finding a number of common points in the studied systems.

First, the binding of the oxygen molecule at the porphyrins induces the electron transfer onto the oxygen species. The bound oxygen molecule becomes negatively charged, thus nucleophilic. It has the highest nucleophilic character while

bound to the molybdenum complex ($q(O_2) = -0.34$), smaller in the manganese porphyrin ($q(O_2) = -0.24$), and the smallest in the cobalt complex ($q(O_2) = -0.14$). It is worth noticing that in the latter case almost the whole negative charge acquired by dioxygen is localized on the outer oxygen atom (Ob).

Second, the analysis of the charge transfers induced by the dioxygen adsorption reveals the important role of the porphyrinato ligand as a source of the electrons in the studied systems. In the case of the Co and Mn compounds the electrons from the porphyrin ring are distributed over the adsorbed oxygen molecule and the metal ions, which leads to the reduction of the metal centers. The largest transfer from the porphyrin ring (0.55e) is observed for the Mn complex, where 0.31e goes to the manganese ion and 0.24e to the adsorbed oxygen molecule. The formation of the end-on species at the Co porphyrin causes the transfer of 0.16e from the porphyrinato ligand onto the cobalt ion and 0.14e onto the oxygen species. The formation of the side-on oxygen species at the Mo porphyrin engages 0.23e from the porphyrin ring and 0.11e from the molybdenum ion, which are directed onto the oxygen molecule.

Finally, spin density analysis performed for the studied systems reveals that the Mn and Mo complexes form the paramagnetic structures with two unpaired electrons located mostly on the metal ions (spin density 2.51 and 1.97, respectively) and partially on the oxygen atoms (each of them is characterized by the spin density equals 0.19 in the case of the Mn porphyrin and 0.17 in the case of the Mo complex). The cobalt porphyrin forms the complex with one unpaired electron located mainly on the dioxygen ligand (spin density 0.99).

While comparing the results of our studies on the dioxygen-bound structures a question arises about parameters of the metal ions which determine their distant behavior in the reaction with dioxygen. The answer to this question is not clear. In this study three different metal ions are studied, each of them being on a different oxidation state (and thus having different charge) but possessing the same coordination environment. It seems that these are the coordination properties of the metal itself that have the largest effect on the coordination mode of the molecular oxygen. For instance, the molybdenum ion, which prefers higher coordination numbers, binds O_2 preferentially as the side-on group, because this way of binding allows it to form a six-coordinate complex rather than a five-coordinate one. This supposition is based on our experience as well as on the experimental evidence[8-10] which suggests that the Mo ion, irrespective of its oxidation state, prefers the formation of the side-on complexes with the O_2 ligand.

Binding of the First Hydrogen Atom. As the next step, the interaction of the hydrogen atom with the molecular oxygen bound to the investigated porphyrin complexes is discussed. Table 4 and Figure 5 summarize the calculated energetic, electronic, and geometric parameters for the studied systems.
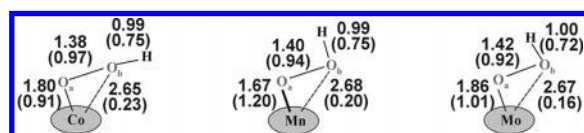
The energies of H binding show that the hydrogen atom becomes stabilized on the oxygen species bound to the porphyrin complex independent of the type of the metal

Table 3. Mulliken Charges on Metal and Oxygen Atoms in the Studied MPO$_2$ Complexes

MP	CoP$-$O$_2$ end-on MULT 2	MnP$-$O$_2$ side-on MULT 3	MoP$-$O$_2$ side-on MULT 3
Q(M)	0.40	0.69	1.34
Q(O$_2$) (Oa; Ob)	−0.14 (−0.02; −0.12)	−0.24 (−0.12; −0.12)	−0.34 (−0.17; −0.17)

Table 4. Binding Energies (E) in [eV] and Charges (Q) Connected with the H Binding at the MPO$_2$ Complexes (M = Co, Mn, Mo)

MP	CoP$-$OOH MULT 1	MnP$-$OOH MULT 2	MoP$-$OOH MULT 2
E_B(H)	−2.78	−2.76	−2.37
E_B(OOH)	−0.93	−0.71	−2.79
E_B(OH)	−2.19	−0.56	0.51
Q(M)	0.44	0.72	1.45
Q(Oa)	−0.24	−0.18	−0.27
Q(Ob); Q(H)	−0.33; 0.44	−0.31; 0.46	−0.34; 0.49
Q(OH)	0.11	0.15	0.15

Figure 5. Bond lengths in [Å] and Mayer bond orders indices (in parentheses) after H binding at the MPO$_2$ systems (M = Co, Mn, Mo).

center (Co, Mn, Mo) and of the geometry of oxygen (side-on, end-on). The energies of the hydrogen binding are similar for the Co and Mn complexes (−2.78 eV and −2.76 eV, respectively) and are higher than for the Mo porphyrin (−2.37 eV).

In the studied porphyrins, the hydrogen atom forms the hydroperoxo group bound to the metal site. The stability of the formed OOH species may be indicated by its binding energy, calculated as a difference between the total energy of the MP−OOH complex and a sum of the total energies of MP and OOH fragments:

$$E_B(\text{OOH}) = E(\text{MP}-\text{OOH}) - [E(\text{MP}) + E(\text{OOH})]$$

The obtained data show that the OOH fragment is stabilized in all studied systems. It is thus thermodynamically not favored to transfer this group to a reactant. In addition, it should be noted that whereas the OOH binding energies are comparable for cobalt and manganese complexes (−0.93 eV and −0.71 eV, respectively), its value is quite high in the case of the molybdenum system (−2.79 eV).

One may also consider the binding of the hydrogen atom as a formation of the OH group bound to the oxo site (M=O). In this respect, the obtained Ob−H bond lengths of 1.00 Å and bond orders of ca. 0.7 are typical for the OH groups. The OH fragments are slightly positively charged, and the charges on OH groups are almost identical in all three systems (ca. 0.15). The stability of the formed OH groups is judged from the OH binding energy calculated according to the formula:

$$E_B(\text{OH}) = E(\text{MP}-\text{O}-\text{OH}) - [E(\text{MP}=\text{O}) + E(\text{OH})]$$

Computed in this way, the OH binding energy is the largest for the CoP porphyrin (−2.19 eV) and smaller for the MnP system (−0.56 eV). In the MoP moiety this is characterized by the positive value (0.51) that suggests the metastable bond.

The changes in geometries induced by the binding of the first hydrogen atom may be described as follows. In the side-on structures (the Mn and Mo systems) the binding of H leads to the breaking of one of the metal−oxygen bonds (between the metal and the Ob atom). Now, only one oxygen atom is connected with the metal center. In the studied systems the OH groups remain bonded with the complexes by the O−O bond, rather than the metal−OH bond. In all structures the metal−OH bond length is equal to 2.7 Å and the bond order amounts to 0.2, whereas the O−OH bonds are characterized by bond orders ca. 0.95 and bond lengths close to 1.4 Å.

The bond between the metal and the second oxygen atom (Oa - not directly connected with hydrogen) does not change significantly in the case of the Co and Mo porphyrins with comparison to the initial structures (see Figures 4 and 5). These are still the single metal−oxygen bonds, characterized by bond orders close to 1. In the case of the manganese system, the formation of the OH group leads to the shortening (from 1.80 Å to 1.67 Å) and the strengthening (the bond orders change from 1.00 to 1.20) of the metal−second oxygen bond. The metal−oxygen bond acquires slowly the character of a double bond.
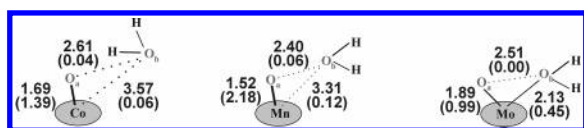
Moreover, the adsorption of hydrogen leads to the further elongation and weakening of the O−O bonds in the Co and Mn porphyrins. The O−O distance increases to ca. 1.40 Å, and the bond orders decrease to ca. 0.95. Only in the case of the Mo system the O−O bond parameters almost do not change after the hydrogen adsorption. The bond length and Mayer bond order indices for MoP system are comparable with their values before adsorption (see Figures 4 and 5).

The delivery of the hydrogen atom results in the oxidation of the metal ions; the largest effect is seen for the Mo porphyrin, where the charge on the metal ion changes from 1.34 before to 1.40 after the hydrogen binding. In the case of the Co and Mn porphyrins, the charge on Co and Mn increases by 0.04 and 0.03 respectively, as compared to the initial complexes with the adsorbed oxygen molecule (see Table 3). In all studied systems, the adsorption of hydrogen leads to the accumulation of the negative charge on both adsorbed oxygen atoms. The charge at the atom connected with hydrogen (Ob) is almost twice as large as compared with the initial complex with the adsorbed oxygen molecule.

The spin density analysis performed for the studied systems reveals that two of the investigated complexes (with manganese and molybdenum ions) are characterized by one unpaired electron in the system. In both cases this is mainly

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Table 5. Binding Energies [eV] and Charges (Q) Describing Binding of the Second Hydrogen Atom at the MPO_2H Complexes (M = Co, Mn, Mo)

MP	CoP−OO2H MULT 2	MnP−OO2H MULT 1	MoP−OO2H MULT 1
$E_B(H^{2nd})$	−3.02		−2.63
$E_B(H_2O)$	−0.15	0.00	3.00
Q(M)	0.44	0.64	1.22
Q(Oa)	−0.42	−0.15	−0.36
Q(Ob); Q(H); Q(H)	−0.88; 0.48; 0.39	−0.78; 0.44; 0.44	−0.81; 0.47; 0.47
$Q(H_2O)$	−0.01	0.10	0.13

Table 6. Energies [eV] and Atomic Charges Characterizing the MPO Species (M = Mn, Mo)

MP	MnP=O MULT 1	MoP=O MULT 3
$E_B(O)$	−3.43	−6.63
Q(M)	0.64	1.51
Q(Oa)	−0.15	−0.35

Figure 7. Bond lengths in [Å] and Mayer bond order indices (in parentheses) for the MP = O species (M = Mn, Mo).

Figure 6. Bond lengths in [Å] and Mayer bond orders indices (in parentheses) after the second H binding at the MPO_2H system (M = Co, Mn, Mo).

located on the central metal ions (spin density equals to 1.04 and 1.27 on Mn and Mo, respectively).

Binding of the Second Hydrogen Atom. In the next step, the adsorption of the second hydrogen atom is studied. Table 5 and Figure 6 show the details of electronic and geometric structure of the formed systems.

The presence of the second hydrogen further differentiates the studied systems; however, a number of similarities may also be find. In all complexes the binding energy of the second hydrogen atom is larger by ca. 0.2 eV than the binding energy of the first hydrogen. The delivery of the second hydrogen promotes a cleavage of the O−O bond; in all complexes the O−O bond length becomes larger than 2.3 Å, and no interaction between the oxygen atoms is observed (bond order indices are close to 0). At the same time, the formation of the water molecule interacting with the porphyrin system is observed. The same as previously, the stability of the formed water species may be indicated by the H_2O binding energy calculated as follows:

$$E_B(H_2O) = E(MP-OOH_2) - [E(MP=O) + E(H_2O)]$$

In the case of the CoP porphyrin the formed water molecule is still bonded to the complex (binding energy −0.15 eV). One of the hydrogen atoms from the water group interacts with the oxygen atom, Oa, bonded to the Co ion by a hydrogen bond. The charge on the Co ion does not change after the binding of the second hydrogen atom. The additional electron is located mainly at both oxygen atoms increasing their nucleophilic character. The Co−Oa bond becomes shorter (by 0.11 Å) and stronger (bond order increases by 0.49) than in the complex with only one hydrogen atom. The analysis of the spin density reveals that the unpaired electron present in this system is delocalized between Co and Oa atoms.

The water molecule formed in the MnP system is not bound to the complex. The water binding energy in the investigated structure is calculated to be 0.0 eV. As a consequence, the bond between the manganese ion and the
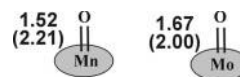
second oxygen atom acquires the character of the double bond, with bond length (1.52 Å) and bond orders (2.18), which are typical for this type of bond.

In the case of the MoP porphyrin the water binding energy is positive (3.0 eV) suggesting its metastable position, but, surprisingly, the distance between the water molecule and the Mo−Oa group is smaller (2.13 Å) than in the other complexes (where it is larger than 3 Å). Moreover, the Mo−Ob bond order which characterizes the bond strength between Mo and oxygen from the water molecule is not negligible (0.45). As a result, the bond between the molybdenum atom and the second oxygen atom (Oa) almost does not change with comparison to the similar bond in the complex with the hydroperoxo group (bond length is equal to 1.9 Å and bond order to 0.99).

Oxo Complexes. The analysis of the energies of OH and H_2O binding in the studied systems suggests that the oxo species may be formed only by the manganese and the molybdenum complexes, as indicated by the positive values of the respective binding energies (see Tables 4 and 5). This finding leads to the conclusion that the negative binding energies of the OH and H_2O species may be the reason for which the cobalt oxo porphyrins are, up to our knowledge, not observed experimentally. That is why only the manganese and molybdenum oxo systems are discussed in the following.

In the case of the manganese porphyrin, the oxygen−metal bond starts to acquire the double bond character just due to the first hydrogen binding (R = 1.67 Å, B.O. = 1.20). After the binding of the second hydrogen and the subsequent formation of the water species (that desorbs from the complex) the parameters characterizing the metal−oxygen bond are almost identical with the parameters calculated for the isolated oxo species (R = 1.52 Å, B.O. = 2.18 vs R = 1.52 Å, B.O. = 2.21, for the MnP−OOH₂ complex and the isolated oxo species, respectively). The same, the electronic parameters such as charges on the metal (0.64) and the oxygen atom (−0.15) are identical with the ones found for the isolated oxo species (see Table 6 and Figure 7).

In the case of the MoP system, for both MoPOOH and MoPOOH₂ systems, the bond between the molybdenum and Oa oxygen atom should be described as the single rather than the double bond. This is indicated by the relatively long Mo−O distance (1.89 Å) and low bond order (0.99). One should mention that the additional calculations performed for the isolated oxo molybdenum compound clearly show

that the double bond is characterized by the bond of 1.67 Å and bond order equal to 2.00.

The complementary information on the studied oxo complexes is delivered by the binding energy of the oxo atom. In the MoP complex, the oxo species binding energy is twice as large as the binding energy of the oxo species in the manganese complex (-6.63 eV vs -3.43 eV, respectively). As a result, the transfer of the oxygen atom toward an organic molecule would be easier from the MnPO species than from the MoPO one.

4. Conclusions

The results of the performed calculations indicate that different catalytically active forms of oxygen (side-on, end-on, hydroperoxo, or oxo) may be formed on the studied porphyrin complexes depending on the type of the central metal. In this respect, the influence of the metal center is clearly visible. It is unclear, however, which are the properties of the metal ion that are responsible for the observed differences. According to our knowledge, these may include such "intrinsic" parameters as electronic configuration or charge as well as "external" ones such as environment (ligands which coordinate to the metal ion). Although in order to better understand their influence, more calculations are needed, and we hope that our study will shed some light on this issue.

It is seen that in the case of the cobalt porphyrin, the active forms of the catalyst would include the end-on complex with dioxygen as well as its hydroperoxo form. Here, the formation of the oxo-group in the described manner would not occur, because the formed water molecule will not easily dissociate from the CoP=O complex, thus disabling its reactivity.

For the manganese complex, on the opposite, there exists a possibility of the formation of the side-on, hydroperoxo, and oxo types of ligands. All of them may be catalytically active and may contribute to the experimentally observed high reactivity of the manganese porphyrins in homogeneous systems.

Finally, the largest variety of the active oxygen species exists in the case of the molybdenum systems. Here, all studied forms that are side-on, end-on, hydroperoxo, and oxo are possible to occur. What is striking, however, is that after the formation of the oxo-complex, the molybdenum tends to increase its coordination number becoming more hindered, and thus its reactivity may be lowered.

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