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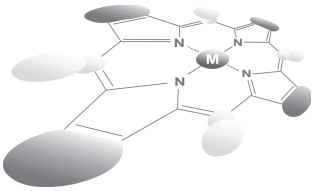


# DFT Quantum-chemical prediction of molecular structure of iron(VI) macrocyclic complex with phthalocyanine and two oxo ligands

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**ABSTRACT:** The possibility of the existence of the unknown iron complex containing phthalocyanine and two oxygen atoms in the inner coordination sphere was predicted using DFT quantum chemical calculation (OPBE/TZVP and B3PW91/TZVP levels). The structural parameters, the ground state multiplicity, the NBO analysis results, and the standard thermodynamic parameters for complex formation (standard enthalpy $\Delta H^0_{f,298}$, entropy $S^0_{f,298}$ and Gibbs's energy $\Delta G^0_{f,298}$) are represented.

**KEYWORDS:** Iron(VI) phthalocyanine, oxo ligand, structural parameters, NBO analysis, thermodynamic parameters, DFT method.

## INTRODUCTION

One of the most important and at the same time very interesting problems of theoretical inorganic and coordination chemistry is the problem of stabilization of chemical compounds in which individual chemical elements are of unusually high oxidation degrees. This problem manifests itself most clearly in the chemistry of 3*d* elements with serial numbers $Z = 26$-30, namely Fe, Co, Ni, Cu and Zn, for which the numerical values of the maximum oxidation degree reliably known at the moment is +7 (in the case of Fe), +6 (in the case of Co), and +4 (in the case of Ni, Cu, and Zn) is less than the total number of electrons in the outer 3d and 4s valence shells (8, 9, 10, 11, and 12, respectively). Compounds of named elements with such oxidation degrees, as a rule, have very low stability; their synthesis presents considerable difficulties, and preliminary theoretical calculations of the molecular structures of these compounds using quantum chemical methods are very useful for its purposeful implementation. Among them, a prominent place belongs to methods based on the density functional theory (DFT), the number of variants of which currently reaches several dozen and which have already proven their effectiveness in calculating the molecular structures of a wide variety of chemical compounds, including those that formed by 3d-elements in general and those listed above in particular. The above also applies to those compounds in which these elements exhibit unusually high oxidation states for them, so that the prospects for using the DFT method to predict the molecular structures and related physicochemical properties of such compounds should not be in doubt.

Among the 3d-elements listed above, the first in number is iron, which currently has a reliably established maximum oxidation degree of +7. Such an oxidation degree takes place in the $FeO_4^-$ anion studied in a recent work [1]. Compounds of this element with an oxidation degree of +6, namely tetraoxoferrates(VI) of *s*-elements, in particular $K_2FeO_4$ and $BaFeO_4$, have been known for a very long time [2–4]. A number of Fe(IV) complexes containing various porphyrin derivatives as ligands are described in the literature (see, f.e. [5–9]). However, according to monographs [10, 11], there is no information about the coordination and macrocyclic iron compounds in which this element would be of such a high oxidation

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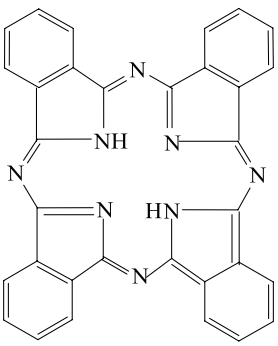
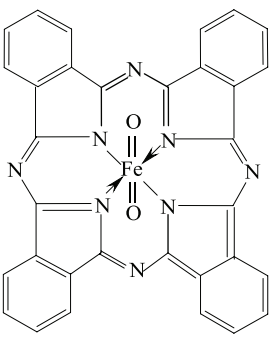
degree. Nevertheless, there is no reason to believe that Fe(VI) complexes cannot exist, and, in this connection, it seems interesting to find such coordination compounds.

It has long been established that such a (NNNN)-donor atomic macrocyclic ligand as tetra[benzo]porphyrazine or phthalocyanine having structural formula **I** (further $H_2$**Pc**) in own double deprotonated form (**Pc**$^{2-}$) capable to stabilize a wide variety of oxidation states of 3*d*-elements – both low and high (see, for example, review articles [12–14] and the books [15, 16]). Another ligand which capable of stabilizing high oxidation degree, is the oxo anion $O^{2-}$ [17–21]. By taking into account the aforesaid, it seems appropriate to use for Fe(VI) stabilization the combination of the given two ligands that occurs in the macrocyclic metal chelate [Fe$^{VI}$(**Pc**)$(O)_2$] with structural formula **II**




**I**




**II**

As indicated above, there is no information on such a metal complex in the current literature; nonetheless, at the present time, a possibility of its existence can be evaluated using modern quantum chemical calculation methods. That is why, this paper will be devoted to consideration of the given problem.

## EXPERIMENTAL

Quantum-chemical calculations were performed by the two versions of DFT method. In the first of them (OPBE/TZVP level), the common TZVP extended triple zeta split-valence basis set [22, 23] and the OPBE non-hybrid functional [24, 25] combined. This version of DFT, as shown in [25–29], in the case of 3*d* elements most adequately predicts the relative energy stabilities of high-spin and low-spin states, and reliably characterizes key geometric parameters of corresponding molecular structures. In the second version, B3PW91/TZVP level, combining the common TZVP basis set and B3PW91 functional described in [30, 31] was used. According to the data [32], this functional has minimal value of so-called "normal error" in comparison with other variants of DFT method. This conclusion is in full harmony with the data of structural parameters of macrocyclic complexes of various 3*d*-elements with phthalocyanine obtained as a result of various DFT quantum-chemical calculations and in experiment (see *supporting information*). All calculations for the iron complex [Fe$^{VI}$(Pc)$(O)_2$] indicated above, were performed with the *Gaussian09* program package [33]. The results of quantum chemical calculations were visualized by means of the *ChemCraft* software, Version 1.8. The correspondence of the found stationary points to energy minima was proved in all cases by the calculation of second derivatives of energy with respect to atom coordinates; all equilibrium structures corresponding to minima of the potential energy surfaces had only real positive frequency values. Theoretically, Fe in the complex under study must have $3d^2$ electronic configuration, and, in this connection, spin multiplicities $M_S = 1$ and $M_S = 3$ were considered in calculation. Among the structures optimized at these multiplicities, the lowest-lying structure was selected. Parameters of molecular structures with the given multiplicities were always calculated by the unrestricted (*UOPBE* and *UB3PW91*) methods. The possibility of the existence of radical cationic forms that can be isostructural [Fe$^{VI}$(Pc)$(O)_2$] complex considered in this paper, was also taken into account in the calculation. In the framework of the both OPBE/TZVP and B3PW91/TZVP methods, if these forms appeared, they had always higher total energy values compared to the [Fe$^{VI}$(Pc)$(O)_2$] complex. In all cases, the wave functions were checked for stability at the minimum point (procedure STABLE = OPT in Gaussian). In all cases, the wave function did not show any features of instability. A calculation of standard thermodynamic parameters of formation of metal complex under study was carried by using methodology presented in the work [34].

## RESULTS AND DISCUSSION

According to the data obtained as a result of our quantum-chemical calculation carried out using the OPBE/TZVP as well as B3PW91/TZVP method, the complex having formula [Fe$^{VI}$(**Pc**)$(O)_2$] is capable of existence as an isolated molecule. The calculated chemical bond lengths between atoms and bond angles for this compound calculated by means of each of quantum-chemical methods indicated above have been presented in Table 1. The image of molecular structure of this complex obtained by one of the given methods, and namely B3PW91/TZVP has been shown in Fig. 1. The image of structure obtained by using OPBE/TZVP method, is very similar with image calculated by B3PW91/TZVP method. As can be seen from the data presented, chelate node FeN4 is ideally plane (in the case of using DFT OPBE/TZVP method) and is practically plane (in the case of using DFT B3PW91/TZVP method). All four 6-membered metal chelate rings, as well as all four 5-membered non-chelate rings containing one nitrogen atom and four carbon atoms and adjacent to 6-membered metal chelate rings in this complex, have a strong planar structure, too. Such a conclusion can be made if we take into account the sum of the bond angles in each of these structural fragments

Table 1. Bond lengths and bond angles in the [$Fe^{VI}$(**Pc**)$(O)_2$] complex calculated by using DFT OPBE/TZVP and DFT B3PW91/TZVP methods.

| Structural parameter | Calculated by DFT OPBE/TZVP | Calculated by DFT B3PW91/TZVP |
|---|---|---|
| **Distances between atoms** | | |
| Fe–N bond lengths in chelate node $MN_4$, *pm* | | |
| Fe1N1 | 197.4 | 195.8 |
| Fe1N2 | 197.2 | 195.1 |
| Fe1N3 | 197.4 | 195.8 |
| Fe1N4 | 197.6 | 195.1 |
| Fe–O bond lengths, *pm* | | |
| Fe1O1 | 163.1 | 168.0 |
| Fe1O2 | 163.0 | 184.6 |
| C–N bond lengths in 6-numbered chelate rings, *pm* | | |
| N1C3 | 136.4 | 135.5 |
| N1C4 | 136.6 | 135.5 |
| N2C1 | 136.5 | 135.8 |
| N2C2 | 136.5 | 135.8 |
| N3C7 | 136.6 | 135.5 |
| N3C8 | 136.4 | 135.5 |
| N4C5 | 136.5 | 135.8 |
| N4C6 | 136.5 | 135.8 |
| N5C2 | 132.2 | 131.8 |
| N5C3 | 132.2 | 131.9 |
| N6C6 | 132.1 | 131.8 |
| N6C7 | 132.2 | 131.9 |
| N7C4 | 132.2 | 131.9 |
| N7C5 | 132.1 | 131.8 |
| N8C1 | 132.2 | 131.8 |
| N8C8 | 132.1 | 131.9 |
| C–C bond lengths in 5-numbered chelate ring (N1C4C9C10C3), *pm* | | |
| C4C9 | 145.8 | 146.5 |
| C9C10 | 140.5 | 139.6 |
| C10C3 | 145.8 | 146.5 |
| **Angles between atoms** | | |
| Bond angles in chelate node $FeN_4$, *deg* | | |
| (N1Fe1N2) | 90.0 | 89.9 |
| (N2Fe1N3) | 90.0 | 89.9 |
| (N3Fe1N4) | 90.0 | 89.9 |
| (N4Fe1N1) | 90.0 | 89.9 |
| Bond angles sum (***BAS***), *deg* | 360.0 | 359.6 |
| Non-bond angles between N atoms in $N_4$ grouping, *deg* | | |
| (N1N2N3) | 90.0 | 90.2 |
| (N2N3N4) | 90.0 | 89.8 |
| (N3N4N1) | 90.0 | 90.2 |

(*Continued*)

Table 1. (*Continued*)

| Structural parameter | Calculated by DFT OPBE/TZVP | Calculated by DFT B3PW91/TZVP |
|---|---|---|
| (N4N1N2) | 90.0 | 89.8 |
| Non-bond angles sum (NBAS), *deg* | 360.0 | 360.0 |
| Bond angles in 6-numbered chelate ring (Fe1N1C4N7C5N4), *deg* | | |
| (Fe1N1C4) | 125.0 | 125.5 |
| (N1C4N7) | 128.5 | 128.1 |
| (C4N7C5) | 123.0 | 122.7 |
| (N7C5N4) | 128.4 | 128.2 |
| (C5N4Fe1) | 125.1 | 125.5 |
| (N4Fe1N1) | 90.0 | 89.9 |
| Bond angles sum (BAS[61]), *deg* | 720.0 | 719.9 |
| Bond angles in 6-numbered chelate ring (Fe1N4C6N6C7N3), *deg* | | |
| (Fe1N4C6) | 125.1 | 125.5 |
| (N4C6N6) | 128.4 | 128.2 |
| (C6N6C7) | 123.0 | 122.7 |
| (N6C7N3) | 128.5 | 128.1 |
| (C7N3Fe1) | 125.0 | 125.5 |
| (N3Fe1N4) | 90.0 | 89.9 |
| Bond angles sum (BAS[62]), *deg* | 720.0 | 719.9 |
| Bond angles in 5-numbered ring (C3N1C4C9C10), *deg* | | |
| (C3N1C4) | 109.8 | 109.0 |
| (N1C4C9) | 108.6 | 109.4 |
| (C4C9C10) | 106.5 | 106.1 |
| (C9C10C3) | 106.5 | 106.1 |
| (C10C3N1) | 108.6 | 109.4 |
| Bond angles sum (BAS[51]), *deg* | 540.0 | 540.0 |
| Bond angles in 5-numbered ring (C1N2C2C12C11), *deg* | | |
| (C1N2C2) | 109.8 | 109.0 |
| (N2C2C12) | 108.6 | 109.3 |
| (C2C12C11) | 106.5 | 106.2 |
| (C12C11C1) | 106.5 | 106.2 |
| (C11C1N2) | 108.6 | 109.3 |
| Bond angles sum (BAS[51]), *deg* | 540.0 | 540.0 |
| Bond angles between O, Fe and N atoms, *deg* | | |
| (O1Fe1N1) | 90.0 | 91.6 |
| (O1Fe1N2) | 90.0 | 92.2 |
| (O1Fe1N3) | 90.0 | 91.6 |
| (O1Fe1N4) | 89.8 | 92.2 |
| (O2Fe1N1) | 90.0 | 88.4 |
| (O2Fe1N2) | 90.2 | 87.8 |
| (O2Fe1N3) | 90.0 | 88.4 |
| (O2Fe1N4) | 90.0 | 87.8 |
| Bond angles between O and Fe atoms, *deg* | | |
| (O1Fe1O2) | 179.8 | 180.0 |

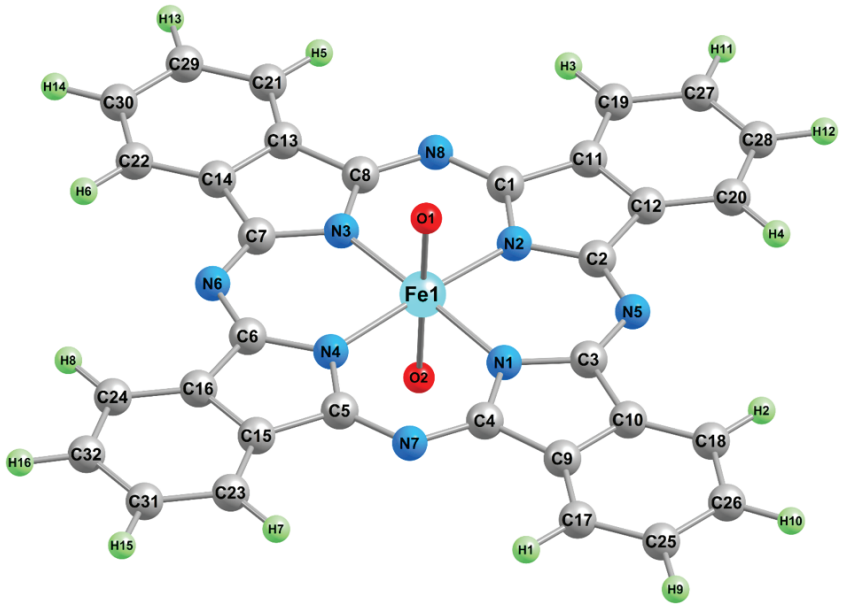



Fig. 1. Molecular structure of the [$Fe^{VI}$(**Pc**)$(O)_2$] complex obtained as a result of DFT B3PW91/TZVP quantum-chemical calculation.

(360.0°, 720.0° and 540.0°, respectively). Besides, both 6-membered chelate rings and 5-membered non-chelate rings are practically identical to each other in the lengths of bonds between the corresponding atoms and in the range of bond angles.

The oxygen and iron atoms in this complex form between themselves an angle of 180.0° (DFT B3PW91/TZVP) or almost or almost indistinguishable from it 179.8° (DFT OPBE/TZVP) (Table 1) and, therefore, are located practically on the same straight line (Fig. 1). On the whole, the structural data obtained by these two independent methods, are in very good agreement with each other, although one cannot but pay attention to some qualitative differences between them. First, there is a rather noticeable difference in the bond lengths between the copper and oxygen atoms (Fe1O1) and (Fe1O2): according to the OPBE/TZVP method, they are practically equal to each other, whereas according to the B3PW91/TZVP method, they are different, although a priori such a difference must not occur. In addition, within the framework of B3PW91/TZVP method, the indicated bond lengths differ by more than 15 pm (Table 1). Also, small difference in the framework of each of these methods takes place between the Fe–N bond lengths; besides, it is again more pronounced in the case of DFT calculation by B3PW91/TZVP method. The fact of such a differences is understandable, since, as it can be easily seen, even with a cursory glance at the structural formula [$Fe^{VI}$(**Pc**)$(O)_2$], the donor nitrogen atoms in the FeN4 chelate node are not equivalent to each other. The totality of all these differences leads to the fact that the electric moments of the dipole (dipole moments) of the complex under examination, calculated by the OPBE/TZVP and B3PW91/TZVP methods, are slightly different from each other (0.01 and 0.06 Debye units, respectively). In this connection, it is interesting to note that with respect to bond angles in 6-membered metal chelate and 5-membered (as well as 6-membered) non-chelated rings, the data of both these calculation methods turn out to be very close to each other. As for the bond angles in the FeN4 chelate node and the angle between iron and oxygen atoms, then their values are close to each other in modulus. However, in the case of the OPBE/TZVP method, most of these angles (6 out of 8) are equal to 90.0°, and the other two differ from this value by only 0.2°; in the case of the B3PW91/TZVP method none of these angles is equal to 90.0°, and the difference in their values is almost 5° (Table 1).

NBO analysis key data are presented in the Table 2, total data can be found in the *supporting information* of this article.

Table 2. NBO analysis data for the [$Fe^{VI}$(**Pc**)$(O)_2$] complex in the ground state according to OPBE/TZVP and B3PW91/TZVP methods.

| | The charges on the atoms, in electron charge units (ē) | | | | | <S**2> |
|---|---|---|---|---|---|---|
| | Fe | N1 (N3) | N2 (N4) | O1 | O2 | |
| OPBE/TZVP | -0.1184 | -0.2864 (-0.2864) | -0.2870 (-0.2878) | -0.0415 | -0.0415 | 0.00 |
| B3PW91/TZVP | 0.0200 | -0.3241 (-0.3241) | -0.3291 (-0.3291) | -0.2941 | -0.3287 | 2.93 |

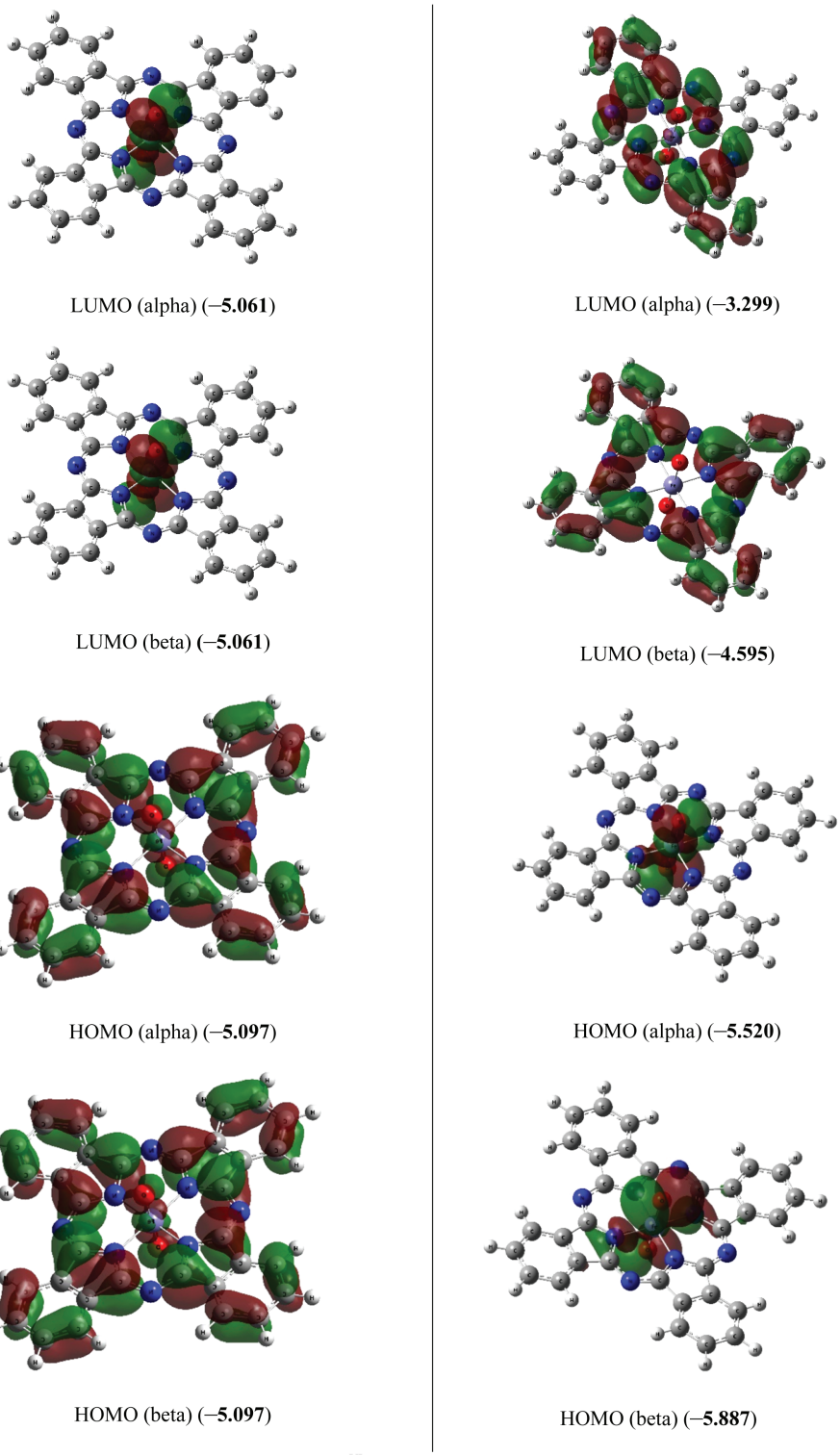



Fig. 2. The pictures of HOMO and LUMO in the [$Fe^{VI}$(**Pc**)$(O)_2$] complex according to the DFT OPBE/TZVP method (*left*) and DFT B3PW91/TZVP method (*right*). The energies values of the given MOs (in brackets) are expressed in eV. The symbol "alpha" belongs to electron having spin (+1/2), symbol "beta", to electron having spin (–l/2).

It is noteworthy that, value of the effective charge on the Fe atom in the [$Fe^{VI}$(**Pc**)$(O)_2$] complex according to the NBO analysis using OPBE/TZVP as well as B3PW91/TZVP method, turns out to be significantly less than +1.00 ē. On the other hand, the effective charges on oxygen atoms differ very significantly from the values (–2.00 ē). This circumstance, and, also, the values of effective charges on other atoms that there are in this chemical compound (in particular, on the N1, N2, N3, and N4 donor nitrogen atoms), is direct indication of the

Table 3. Standard thermodynamic parameters of formation for [$Fe^{VI}$(**Pc**)$(O)_2$] complex calculated by OPBE/TZVP and B3PW91/TZVP methods.

| Calculation method | $\Delta H^0_{f,\ 298}$, kJ/mole | $S^0_{f,\ 298}$, J/mole · K | $\Delta G^0_{f,\ 298}$, kJ/mole |
|---|---|---|---|
| OPBE/TZVP | 337.6 | 1157.9 | 599.3 |
| B3PW91/TZVP | 949.6 | 1142.5 | 1215.9 |

very high degree of electron density delocalization in the given metal complex. The images of highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of iron compound under examination are presented in Fig. 2.

According to the data of our calculations, the ground state of the [$Fe^{VI}$(**Pc**)$(O)_2$] heteroligand complex in the framework of the OPBE/TZVP method is a spin singlet. According to the data of this method, the nearest excited quartet state has much higher energy (59.1 kJ/mol). Such a situation is not typical for tetragonal (pseudo-octahedral) complexes with having $3d^2$ electron configuration, and a coordination number of a metal ion equal to 6. B3PW91/TZVP method, however, gives an inverse relationship: the ground state is a spin triplet, while the nearest singlet state has an energy 21.6 kJ/mol higher. Taking into account the fact that according to numerous statistical data for complexes with the configuration $d^2$, having coordination number 6 and $D_{4h}$, $C_{2h}$ or $C_{2v}$ symmetry group, the ground state is precisely the spin triplet, the result obtained by the B3PW91/TZVP method seems to be more reliable. It is interesting that, within the framework of this method, the next excited state in terms of energy is not a singlet, but a quintet, and the energy difference between it and the main triplet is only 0.2 kJ/mol, so that a spin crossover may well take place here.

The standard thermodynamic parameters of formation for the given macrocyclic metal chelate under examination ($\Delta H^0_{f,\ 298}$, $S^0_{f,\ 298}$ and $\Delta G^0_{f,\ 298}$) have been presented in Table 3. As can be seen from it, all are positive.

Hence, such a complex cannot be obtained from the simple substances formed by chemical elements having in their compositions (i.e. C, N, O, and Fe). Nevertheless, according to the data obtained as a result of the quantum-chemical calculation carried out by us, the molecular structure of [$Fe^{VI}$(**Pc**)$(O)_2$] compound and the full totality of their geometric parameters, it can be realized as a single whole (i.e. as an isolated molecule). Thus, it can be argued that the given complex is capable to existence, at least in the gas phase as individual molecules.

## CONCLUSION

As can be seen from the above data, both variants of the DFT method that we used, namely OPBE/TZVP and B3PW91/TZVP, unambiguously predicted the possibility of the existence of [$Fe^{VI}$(Pc)$(O)_2$] complex where $Pc^{2-}$ is double deprotonated form of phthalocyanine. If so, in accordance with the generally accepted definition of the term "oxidation degree", and namely "the oxidation degree is the charge in units of electron charge that would occur on the atom of a given element in a given chemical compound under the assumption that within the framework of each of the conditionally existing in this compound two-center two-electron chemical bonds formed by the exchange mechanism, there would be a complete transfer of electrons from the atom with less electronegativity to the atom with more electronegativity" [35], we can assume that the oxidation degree of the central atom in the complex under study, and namely Fe, is +6, since in it, there are six bonds formed by atom of the given element with atoms having greater electronegativity in comparison with it, according to the exchange mechanism, and namely – two with nitrogen atoms and four with oxygen atom. Since the oxidation state of any chemical element with a positive oxidation degree is determined as the modulus of the given parameter and is displayed by the corresponding *Roman numeral*, in this complex, the oxidation state of iron is namely VI. Another thing is that the real charge on the Fe atom in it differs significantly from the value of +6.00 ē, but such a parameter has not been connected with the above definition and, if so, then in principle it cannot be used for definition of the oxidation state. In the connection with aforesaid, it is important to confirm now an existence of this macrocyclic metal complex experimentally.

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**Supporting information**

The bond lengths, bond and non-bond angles in the phthalocyanines complexes of 3d-elements and, also, the data of NBO analysis of [$Fe^{VI}$(Pc)$(O)_2$] compound under study, are given in the supplementary material. This material is available free of charge *via* the Internet at https://www.worldscientific.com/doi/suppl/10.1142/S1088424622500274

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