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Models for the adsorption of dioxygen on metal chelates[#]

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Abstract. Metal chelates are suitable electrocatalysts for the reduction of dioxygen. The selectivity of the reduction process (H_2O_2 or H_2O as end product) depends on which catalyst is used. Comparable compounds, such as cobalt and iron phthalocyanine (CoPc and FePc), show different selectivities. CoPc catalyzes the dioxygen reduction pathway with H_2O_2 as the end product, whereas FePc gives H_2O . The interaction between the catalyst and dioxygen is crucial for the selectivity of the reduction process. In this review, the most important models for the adsorption of dioxygen on metal chelates are discussed.

Most of these models predict that dioxygen is adsorbed in a so-called “end-on (bent)” configuration on to the metal phthalocyanines. The models also predict that, for the dioxygen adduct of CoPc, the oxygen fragment is more negatively charged than for the adduct of FePc, and that this may be the reason for the observed difference in selectivity. Alternatively, dioxygen can bind in between two metal phthalocyanine molecules. For these dioxygen-bridged dimers, as can be derived from adsorption (bonding) models, the cleavage of the oxygen–oxygen bond occurs more easily in the case of the FePc dioxygen dimer than in the corresponding Co complex.

Introduction

Metal chelates, especially CoPc and FePc, are interesting electrocatalysts for the reduction of dioxygen in, for example, fuel cells. In a fuel cell, the metal chelates are adsorbed on to a conducting material, such as carbon. Dioxygen can adsorb on to the modified electrode surface.

The interaction between both should be weak to allow for an acceleration of dioxygen reduction. For these reasons, the association of dioxygen with the metal chelate can be described as an adsorption process, as is commonly reported for published electrochemical data on dioxygen adsorption. However, in case of metal chelate and dioxygen, a description in terms of covalent bonds is also possible. We prefer to use the term “adsorption”, but sometimes the alternative description in terms of covalent bonds is used.

As has been stated above, two different dioxygen reduction pathways are possible. (1) As occurs with CoPc, dioxygen is reduced to hydrogen peroxide by accepting two electrons. (2) With FePc a reduction to water occurs, with the circumvention of hydrogen peroxide and the acceptance of four electrons per dioxygen molecule. The fundamental difference between the pathways has been the subject of many electrochemical studies^{1a–i}. The selectivity of reduction for each catalyst can then be defined as the ratio between produced water and produced hydrogen peroxide.

It is to be expected that the dioxygen adduct formed and its

properties are essential for determining the type of the reduction process. Therefore, some models for the description of the dioxygen adducts of metal phthalocyanines will be reviewed here.

A number of extensive reviews are available on dioxygen binding to metal complexes (e.g., Gubelmann and Williams^{2a}). In this review, the dioxygen adducts of metal phthalocyanines will be discussed, in particularly with respect to dioxygen reduction.

Most of the proposed models, have been developed to explain a specific aspect (e.g., ESR signal) of the dioxygen binding to the metal chelates. A number of theoretical studies have also focussed on dioxygen adsorption on porphyrin-type chelates, because iron porphyrin (FeP) is considered to be the active centre of the hemoglobin molecule^{2b}. These studies will also be discussed, because of the resemblance of these chelates to phthalocyanines.

Dioxygen can also be adsorbed as a bridge between two metal ions, belonging to two different metal phthalocyanine molecules. Therefore, dioxygen adducts of binuclear metal complexes are also considered.

The Molecular Orbital (MO) description of dioxygen and a description of a metal chelate in the ligand field approximation, are given first. Qualitative models followed by quantitative calculation models will then be discussed.

Electronic structure of dioxygen and of a metal chelate

The energy-level diagram of dioxygen molecule can be derived via the MO method. Although well known, a short

[#] Dedicated to Prof. Dr. W. Drenth on the occasion of his retirement from the Chair of Physical Organic Chemistry at the University of Utrecht.

description is given here to define the symbols used (see Figure 1). In the ground state, the molecular orbitals are occupied such that two unpaired electrons are in the two degenerated anti-bonding π orbitals³. Therefore, the ground state is a triplet state and can be denoted by $^3\Sigma_g^-$. In the diagram, three bonds are shown: a two-electron σ bond: $(3\sigma_g)^2$ and two three-electron π bonds: $(1\pi_u)^2(1\pi_g)^1$.

Fig. 1. MO diagram of dioxygen.

The crystal-field or the ligand-field theory (in some cases, it is more convenient to use this latter approximation) predict the energy-level scheme for the d orbitals of a transition metal, surrounded by ligands^{4,5}. For metal phthalocyanines (MePc), the four ligands (the most inner nitrogen atoms of the phthalocyanine ring structure) are coordinated to the metal in a square-planar geometry. In Figure 2, only for the

Fig. 2. Energy-level diagram for 3d-metal orbitals in several geometries.

sake of completeness, the level splitting expected for these planar complexes is given. In this Figure, the patterns of splitting for the octahedrally and tetragonally distorted octahedral complex are also given; for the latter, a fifth ligand is necessary. When MePc is deposited on to an electrode, basic surface groups of the substrate, or water, or even another dioxygen molecule, may act as a fifth ligand for the metal ion⁶. The ligand-field theory predicts a general energy-level diagram for the various geometries. In individual cases, depending on the type of ligand and metal ion, some deviations from the general pattern are possible.

The next problem is: how do the electrons spread themselves over the orbitals of the diagram? Hund's rule predicts, other conditions being equal, that the states of the highest spin will have the lowest energy⁷. In this simple model, CoPc and FePc are complexes with a strong ligand field, which means that the energy-level splitting is such that the spins are paired as much as possible⁸. Thus, in principle, MePc's are low-spin complexes. The presence of a fifth ligand only affects the occupation of the d_{z^2} and d_{xy} orbitals and has, therefore, no influence on the spin multiplicity of CoPc. However, for FePc, it is possible that

coordination of an extra fifth ligand causes a spin-multiplicity change from low to intermediate or even to high spin.

Electronic structure of dioxygen adducts.

Qualitative models

One of the first models for dioxygen adsorption on to metal complexes was proposed by Griffiths⁹. In his model, he assumes sp^2 hybridization for the oxygen atom close to the metal ion^{3,10}. When the geometry is as in Figures 3a and 3b, the sp^2 orbital χ can be described by:

$$\chi = \frac{1}{\sqrt{3}} \cdot \psi(2s) - \frac{1}{\sqrt{2}} \cdot \psi(2p_x) + \frac{1}{\sqrt{6}} \cdot \psi(2p_y) \quad (1)$$

The ionization energy of this orbital can be calculated from those of the atomic orbitals by using $\frac{1}{3}$ of the value for the $2s$ orbital and $\frac{2}{3}$ of the value for the $2p$ orbital. From the atomic spectra of oxygen, an ionization energy of 0.216 kJ/mol is calculated for the orbital χ . For the alternative structure (see Figure 3b), Griffiths found an ionization

Fig. 3. Adsorption types of dioxygen: (a) "end-on" (sp^2 orbital); (b) "side-on" ($1\pi_u$ orbital).

energy of 0.172 kJ/mol from molecular spectra for the $1\pi_u$ molecular orbital. This difference led him to the conclusion that the last structure is the most favourable one because, in this structure, the electrons of dioxygen are more easily involved in the oxygen-metal bond than for the structure shown in Figure 3a. (The dioxygen orbitals are considered to be donating orbitals.) The two adsorption types depicted in Figures 3a and 3b are called "end-on" (bent) and "side-on" adsorption, respectively. Griffiths came to the conclusion that dioxygen always adsorbs in the "side-on" configuration and, hence, this type of adsorption is often called "Griffiths" adsorption. This model has the advantage that it presents a simple physical picture of dioxygen adsorption, but it is too crude because of the complete neglect of the metal atomic orbitals. Comparison between the atomic and molecular orbitals is also questionable.

"End-on" adsorption was first proposed by Pauling^{11,12}. Using the same concepts described above, an extension of the Griffiths model can be made by also considering the metal atomic orbitals¹⁰. For a transition metal in a relatively high oxidation state, the d orbitals will be considerably contracted, compared with the zero-valent state; thus, the overlap with the bonding and anti-bonding π orbital of dioxygen will be small in the "side-on" adsorption case. Therefore, the dioxygen ligand coordinated to iron(II) and cobalt(II) complexes prefers the "end-on" orientation. For the charges on the dioxygen ligand and the metal ion, Weiss¹³ proposed that the dioxygen in oxyhemoglobin is present as superoxide ion, with the iron being in the ferric state, i.e., $\text{Fe(III)}-\text{O}_2^-$.

The following, more sophisticated model to discuss is the

*spin-pairing model*¹⁴⁻¹⁶. The pertaining theory has both qualitative and quantitative aspects, and is developed to explain the results of ESR spectroscopy. In the spin-pairing model, the metal ion and dioxygen molecule are both considered to be free radicals, whose spins have paired up in the dioxygen adducts¹⁴. In this context, *Drago and Corden*¹⁴ describe the binding of dioxygen to five-coordinated cobalt(II) complexes (within the framework of this spin-pairing theory). The energy-level diagram of the cobalt(II) complex is given in the left part of Figure 4. The level-splitting pattern is

Fig. 4. Energy-level scheme for dioxygen bonding to a Co(II) complex within the spin-pairing model. Only stabilizing interactions are depicted.

predicted by simple ligand-field theory and is, of course, the same as given in Figure 2 for the tetragonally distorted octahedral complex. A $1\pi_g$ orbital, which contains one of the two unpaired dioxygen electrons, overlaps with the d_{z^2} orbital of the cobalt(II) ion. This results in a σ bonding orbital containing two electrons. The corresponding σ^* antibonding orbital is empty. The other $1\pi_g$ orbital is orthogonal to the d_{z^2} orbital and remains essentially unaltered in the adduct. The unpaired electron of the adduct resides in the unaltered $1\pi_g$ orbital and belongs mainly to the dioxygen molecule. To maximize to σ bonding interaction between the d_{z^2} and the $1\pi_g$ orbitals, the adduct tends to have a bent configuration, as shown in Figure 4¹⁶. The overlap of other d orbitals with dioxygen molecular orbitals is neglected in this model.

As already mentioned before, the spin state of iron(II) porphyrin or phthalocyanine complexes can change easily. It is often reported that coordination of an axial base to a four-coordinated iron(II) complex converts the complex into a high-spin complex which, thereafter, reversibly picks up dioxygen^{10,14,17-19}. Therefore, in the spin-pairing model,

Fig. 5. Energy-level scheme for dioxygen bonding to a Fe(II) complex within the spin-pairing model: (a) "end-on (bent)" adduct; (b) "end-on (linear)" adduct. Only stabilizing interactions are depicted.

high-spin five-coordinated iron(II) is used as the starting point. From the energy-level schemes of the iron ion and the dioxygen molecule, as depicted in the left and right parts of Figure 5, respectively, two types of molecular-orbital schemes can be constructed for the dioxygen adduct: the first is given in Figure 5a: the metal d_{z^2} orbital overlaps with one of the anti-bonding $1\pi_g$ dioxygen orbitals. The combination results in a filled σ bonding and an empty σ^* antibonding orbital. One of the d_{xz} or d_{yz} orbitals is also partly occupied and the orbitals can overlap with the other anti-bonding $1\pi_g$ orbital of the dioxygen molecule to form a bonding and anti-bonding combination with π symmetry ($d\pi-p\pi$). The occupancy of the molecular orbitals is also given in Figure 5a. All levels are either fully populated or empty and, therefore, the adduct is diamagnetic, as is observed for reversible iron(II) systems¹⁵.

An overlap of both $1\pi_g$ orbitals with the d_{xz} and/or d_{yz} orbitals is also possible. The d_{z^2} orbital is now raised in energy by its strong interaction with the dioxygen ligand. This interaction is thought to be so strong that the d_{z^2} orbital is driven higher in energy than the $d_{x^2-y^2}$ orbital (see Figure 5b). The level scheme now shows two fully populated ($d\pi-p\pi$) bonding and two empty ($d\pi-p\pi$) anti-bonding combinations. This formalism of the dioxygen binding to the iron(II) complex also leads to a diamagnetic complex.

For the first formulation, an adduct is expected with geometry which lies between the linear and bent configurations. For the latter case, with only $d\pi-p\pi$ interactions, a linear adduct is favoured, because this geometry results in maximum possible overlap between the metal d_{xz} , d_{yz} and dioxygen $1\pi_g$ orbitals¹⁶ (see Figure 5). Although a linear complex is possible within the spin-pairing model, a bent dioxygen adduct has been reported for most iron(II) porphyrin complexes¹⁶.

Another important theory is the *increased valence theory*^{20,21}, as applied by *Harcourt* to dioxygen-bridged dimers of porphyrins²². *van der Putten*²³ used this theory to explain the dioxygen-reduction behaviour of a planar dicobalt chelate. Only the principles of the increased valence theory are outlined here. In the dioxygen-bridged dimers of porphyrins, "bridge" adsorption of dioxygen occurs²⁴. The dioxygen molecule interacts here with two metal atoms simultaneously, see Figure 6 (*cf.*, with the "side-on" and "end-on"

Fig. 6. Various adsorption types of dioxygen.

adsorption types). For noble metals, such as platinum and silver, bridged adsorption is often assumed^{25,26}. In the cofacial dicobalt porphyrins synthesized by *Collman* and coworkers²⁷, the porphyrin rings are interconnected with two chains of atoms. For a chain of four atoms, the distance created between the two cobalt ions makes bridge interaction with the dioxygen molecule possible.

The increased-valence theory can be considered as an extension of the classical valence theory. Some quantum-chemical concepts about one-electron bonds (for instance, H_2^+) are added to the normal two-electrons bonds (electron-pair bonding) of the valence theory. The increased valence formulae are constructed from the normal valence formulae, but now the possibility that electrons occupy anti-bonding orbitals is also accounted for in the formulae. The

theory is convenient for description of a molecular system in which four electrons are delocalized over three atomic orbitals, belonging to three different atoms. (In the case of a dioxygen adduct, the three atoms are the metal and two oxygen atoms, respectively.) A more extensive treatment of the theory is given by *van der Putten*²³.

Electronic structure of dioxygen adducts. Quantitative models

A further theory can be denoted as the *spin-crossover theory*, which is based on a semi-quantitative model. After dioxygen adsorption on to an iron-chelate molecule, resonance between the following configurations is possible²⁸:

Appleby and coworkers proposed that, in the bulk of, for instance, a vacuum-deposited layer of iron phthalocyanine, the following chemisorption step occurs²⁹:

From results of several spectroscopic techniques, such as Mössbauer and Optical Reflectance Spectroscopy, it can be concluded that the chemisorption of dioxygen is most favourable for Fe(III) high-spin or intermediate-spin configurations. Likewise, *Appleby* et al. explained the conduction mechanism of the phthalocyanine layer by supposing resonance (with chemisorption) and the existence of complete redox chains in the layer, in which charge transfer occurs by the following:

Appleby et al. assumed that the existence of an easy multi-spin crossover is an important factor for a complex to bind dioxygen and to catalyse its reduction²⁸. This assumption is based on the above equations in which, for dioxygen, both singlet and triplet states are possible.

The ground-state wave functions (or vectors) for the $d^5(\text{Fe}^{3+})$ configuration in N_4 chelates have been determined³⁰. A short description of the calculation technique will be given, focussed on the method to decide from ESR data whether spin crossover occurs easily or with difficulty for a certain complex.

The angular-momentum quantum numbers of the individual electrons (l) and the spin quantum numbers of the individual electrons (s) can be added to one angular-momentum quantum number L and one spin quantum number S . The following terms ($^2S + ^1L$) can then be derived for the d^5 configuration: $^6S, ^4P, ^4D, ^4G, ^2S, ^2P, ^2D, ^2D, ^2F, ^2F, ^2G, ^2H, ^2I$. The energies of these terms are determined by inter-electronic repulsion. The spin-orbit coupling must now be accounted for and a new quantum number $J = L + S$ can be defined (weak coupling limit). At this stage, the derived wave functions (or states) are orthogonal and are composed of functions which can be defined by SLJ . These are the ordinary states of the free ion.

The degeneracy of the states is further reduced through the crystal-field operator. This operator can be expanded in spherical harmonics; for an octahedral, we have:

$$V(r) = - \sum_{i=1}^6 \frac{Z_i \cdot e^2}{|R \cdot i - r|} = - \sum_{i=1}^6 \sum_{n=0}^{\infty} \sum_{m=-n}^n \left[\left(\frac{4\pi}{2n+1} \right) \cdot \left(\frac{Z \cdot e^2 \cdot r^n}{a^{n+1}} \right) \cdot C_m^n(\theta, \phi) \cdot C_m^n(\theta_i, \phi_i) \right] \quad (5)$$

where Z_i is the charge of the ligand on the place R_i , e is the unit of charge, $C_m^n(\theta, \phi)$ are the spherical harmonics, a is the distance of the ligands from the origin and (r, θ, ϕ) are the coordinates of the electron. For C_{4v} symmetry, the crystal-field operator can be simplified to:

$$V = B_0^2 \cdot C_0^2 + B_0^4 \cdot C_0^4 + B_4^4 \cdot (C_{-4}^4 + C_4^4) \quad (6)$$

where B_i^j are crystal-field parameters. The Hamiltonian can be diagonalized for several combinations of the crystal-field parameters. The resulting ground-state wave functions remain reasonably well characterized by the spin quantum number. Ground-state spin diagrams can now be constructed, in which the ground-state spin multiplicity is given as a function of the crystal-field parameters.

For the ground-state wave functions of each spin-multiplicity domain, it is possible to calculate the electron g values, which can be compared with the g values measured by ESR spectroscopy. In this way, the place of a complex in the ground-state spin diagram can be determined. An easy spin crossover can be expected when the complex lies close to the border between two multiplicities. In short, the procedure is as follows: for a Fe(III) complex, the g values are determined by ESR spectroscopy. The wave function which belongs to these g values and its place in the ground-state spin diagram are determined. When the complex lies on the border of two multiplicities, it is expected that the complex is active in dioxygen reduction.

Three g values, instead of two as for C_{4v} symmetry, are found for many Fe(III) complexes. This indicates that the symmetry of the complex is even lower than C_{4v} symmetry. To account for this, the above calculation must be repeated for C_{2v} symmetry.

One of the first quantum-chemical calculations on iron porphyrin (FeP) was published by *Zerner* et al.³¹. To perform these calculations, the Hückel approximation was adapted until a method resulted which was suitable to calculate the energies of the d orbitals of the metal ion in the ligand field of the macrocycle.

The result of the calculations is a sequence in increasing energy for the metal d orbitals: $d_{xy} \leq d_{xz}, d_{yz} \leq d_{z^2} \leq d_{x^2-y^2}$. In most cases, this sequence did not change when they added a fifth (axial) ligand such as, for instance, water, to the calculation model. The position of the iron ion (above or in the plane of the molecule) also did not change the energy order of the d orbitals. These modifications can, of course, change the energies of the orbitals and this influences their occupancy.

An FeP molecule with the Fe atom in the plane of the macrocycle resulted, in this model calculation, in an intermediate ($S = 1$) spin state with the occupancy: $(d_{xy})^2; (d_{xz}, d_{yz})^3; (d_{z^2})^1; (d_{x^2-y^2})^0$. For the iron atom above the plane of the ligand, *Zerner* et al.³¹ found a high ($S = 2$) spin state, which belongs to the occupancy: $(d_{xy})^2; (d_{xz}, d_{yz})^2; (d_{z^2})^1; (d_{x^2-y^2})^1$.

When the adduct formation of dioxygen is treated within the same model, a "side-on" adsorption geometry for the adduct is predicted and the molecular orbitals are filled such that the dioxygen is diamagnetic.

The "end-on" adsorption appeared not to be stable within this extended Hückel calculation model.

The same approximation method has been applied to metal phthalocyanines (MePc) by *Schaffer* et al.³². The cage formed by the four nitrogen atoms is somewhat smaller for these complexes than for porphyrin complexes. This leads to degeneration of the d_{xy} orbital, because the lobes of this orbital are pointing towards the nitrogen atoms of the ligand. To deal with this, a bonding and an anti-bonding combination of the d_{xy} orbital and the ligand orbitals can be constructed. These orbitals are denoted by d_{xy} and d_{xy}^* .

respectively. The authors proposed, on the basis of this calculation, the following sequence in increasing energy for the d orbitals: $d_{xy} \leq d_{xz}, d_{yz} \leq d_{z^2} \leq d_{xy^*} < d_{x^2-y^2}$. ESR measurements showed that the unpaired electron of CoPc is placed in the d_{z^2} orbital instead of the d_{xy^*} orbital, as would be expected by using the above energy order. Schaffer et al. give as possible explanation that, in a phthalocyanine crystal, the nitrogen atoms of the neighbouring molecules, in adjacent layers above and below the phthalocyanine molecule, act as fifth (or sixth) ligands and drive the energy of the d_{z^2} state above that of the d_{xy^*} state. For FePc, the d_{xy^*} orbital is also occupied before d_{z^2} . A planar FePc molecule is proposed, with an intermediate ($S = 1$) spin state. A high ($S = 2$) spin complex is not attainable with FePc, because this requires displacement from the molecular plane considerably further than for the corresponding FeP complex. This will weaken the iron–nitrogen bonds too much and, thus, makes the high-spin complex energetically unfavourable.

A related compound to the phthalocyanines is cobalt-BPED*, for which the structure is given in Figure 7³³. Two

Fig. 7. The molecular structure of cobalt-BPED.

of the four inner nitrogen atoms of the phthalocyanine complex are replaced by oxygen atoms. Rohmer et al.³⁴ have carried out calculations to decide whether the dioxygen adsorption on the cobalt ion is "end-on" or "side-on". From ESR measurements with ¹⁷O-labeled dioxygen, it can be concluded that both oxygen atoms are magnetically equivalent. This result is consistent either with a "side-on" structure or with a rapid flipping of the dioxygen group between two bent positions. The oxygen atoms rearrange as shown in Figure 8.

Fig. 8. Flipping of the dioxygen group between two "end-on" geometries.

The result is that, for "end-on" adsorption, an average "side-on" structure is also observed. Although the average structure is the same for both adsorption types, there is one fundamental difference: the average "side-on" structure represents, for the "end-on" adsorption, an energy maximum, whilst for the "side-on" adsorption, this implies a minimum of energy.

Calculations by Rohmer et al.³⁴ showed that "end-on" adsorption is the most stable configuration. The introduction of a fifth axial ligand on the cobalt ion did not alter the energy sequence for the two adsorption types.

Rohmer et al.³⁴ also described the general principles and interactions which determine the energies of the various

ways of adsorption. Since a great part of this treatment is also valid for phthalocyanine molecules, the case of cobalt-BPED will now be considered. In the model calculation, the atomic orbitals of the involved atoms are used as starting points. The $2p_x$ and $2p_z$ atomic orbitals of oxygen are composed to a new orbital, denoted by π_g^a (or π_g^b , depending on the overlap between the orbitals of the two oxygen atoms). Only the atomic orbitals of oxygen are given, such that an easy description of the overlap between the involved orbitals is possible for the adsorption geometries shown in Figures 9–11. It should be noted that superscript "a" does not indicate that the orbital is anti-bonding. For some adsorption geometries, this orbital consists almost entirely of the $2p_z$ atomic orbital, whereas for other cases, it is an equal mixture of the $2p_z$ and $2p_x$ atomic orbitals. The remaining $2p_y$ orbital of the oxygen atom is denoted π_g^b . These $2p$ orbitals also participate, of course, in the oxygen–oxygen bond; the normal MO diagram for dioxygen, as given in Figure 1, remains valid. For the metal ion, the normal d orbitals are used. In Figures 9–11, the orbital overlap is drawn for "end-on" (bent), "end-on" (linear) and "side-on" adsorptions, respectively. The strength of a bond is predicted not only by the overlap between two orbitals but also by the energy difference and occupancy level of the orbitals.

For cobalt-BPED, the order in increasing energy for the d orbitals is: $d_{xy} \leq d_{xz}, d_{yz} \leq d_{z^2} \leq d_{x^2-y^2}$, whereas according

Fig. 9. Orbital overlap for "end-on (bent)" adsorption. To draw the d_{yz} and $1\pi_g^b$ orbitals, the axes are rotated 90° counter clockwise.

Fig. 10. Orbital overlap for "end-on (linear)" adsorption. Other conditions as in Figure 9.

* BPED = bis(2,4-pentanedione) ethylenediimine.

Fig. 11. Orbital overlap for "side-on" adsorption. Other conditions as in Figure 9.

to Rohmer et al.³⁴, the d_{z^2} orbital has a higher energy than the anti-bonding $1\pi_g^b$ orbital of dioxygen. This metal d_{z^2} orbital overlaps in the "end-on" (bent) geometry with $1\pi_g^a$, for the "end-on" (linear) case with $3\sigma_g$ and for the "side-on" structure with the bonding $1\pi_u^a$ orbital of the dioxygen molecule (see Figures 9–11).

For these orbitals, the smallest energy difference can be expected between the d_{z^2} and the anti-bonding $1\pi_g^b$ orbitals; therefore, this combination has the most stabilizing effect on the adduct. The interactions of the metal d_{xz} and d_{yz} with the MO orbitals of dioxygen are comparable for the two "end-on" adsorption cases. Thus, the "end-on" (bent) structure is more favourable than the linear one. In the "side-on" adsorption structure, the d_{yz} orbital overlaps with the bonding $1\pi_u^a$ orbital of the dioxygen molecule and, because both orbitals are filled, this overlap destabilizes the adduct (see Figure 11).

When the same concepts are used for cobalt phthalocyanine, an "end-on" (bent) structure is predicted for its dioxygen adduct, if at least the metal d_{z^2} orbital of this complex is also in an energy state above that of the $1\pi_g$ orbital of the dioxygen molecule.

In the last decade, several *ab-initio* calculation methods have been developed to reveal the electronic structure of porphyrins and of their dioxygen adducts. Especially, the dioxygen adduct of an iron porphyrin was often a subject of study, because this compound, is considered to be a model compound for the active centre of the hemoglobin molecule. Many research workers are also puzzled by the observed cooperativity phenomenon for the hemoglobin molecule. The molecule possesses four iron-porphyrin groups and, after dioxygen adsorption on one of these, the others are activated to also adsorb a dioxygen molecule³⁵. In normal deoxyhemoglobin, the iron ion is displaced out of the plane of the porphyrin ring and this out-of-plane displacement has been estimated from an X-ray diffraction study³⁶ to be 0.06 nm. When dioxygen binds to deoxyhemoglobin, the iron ion moves into the plane of the porphyrin ring and, by a proposed sequential process, causes conformation changes in the four heme subunits. These changes are held to be responsible for the cooperativity of dioxygen bonding to hemoglobin^{37,38}.

Many quantum-chemical calculations have been performed in attempts to reveal the mechanism of the movement of the iron ion in iron porphyrin into the plane of the porphyrin ring as a result of dioxygen adsorption³⁹. Only the electronic structures of the dioxygen adducts of cobalt and iron porphyrin predicted by most of these methods will be considered here. For the dioxygen adduct of cobalt porphyrin, with NH_3 as fifth (axial) ligand, the energy sequence and occupancy of orbitals was calculated by Dedieu et al.³⁹ to be:

$$(d_{xy})^2 \cdot (d_{xz})^2 \cdot (d_{yz})^2 \cdot (\pi_g^a)^2 \cdot (\pi_g^b)^1.$$

Here, π_g^a and π_g^b have the same meaning as in the discussion of the electronic structure of cobalt-BPED. NH_3 is also used in many computations to simulate the effect of imidazole. In biological systems, this base is often encountered as a fifth (or sixth) axial ligand to the porphyrin¹⁹. For a catalyst, such as CoPc or FePc, adsorbed on to graphite, basic groups of the surface probably occupy the fifth axially coordination site as already stated; dioxygen can, therefore, bind to the sixth coordination place^{40,41}.

Therefore, the dioxygen binding to four- (as well as to five-) coordinated CoPc should be examined. The ground-state electronic configuration, indicates a charge transfer from cobalt to the dioxygen group, and a formal description, such as $\text{Co(III)}-\text{O}_2^-$, is possible for the cobalt porphyrin-dioxygen adduct. Another result of the calculations of Dedieu³³ is that the "end-on" (bent) structure is the most favoured one. This was confirmed by recent calculations by Newton et al.⁴² for $\text{Co(O}_2\text{)P} \cdot \text{NH}_3$.

Several authors give a ground-state configuration for $\text{Fe(O}_2\text{)P} \cdot \text{NH}_3$ which corresponds with the formal description of the system, as Fe(II)O_2 , i.e., a neutral dioxygen group^{39,43–45}. From Mulliken population analysis, a neutral dioxygen group is obtained but, according to Case et al.⁴⁴, a net negative charge for the dioxygen unit results. Most of the *ab-initio* calculations predict a bent $\text{Fe}-\text{O}-\text{O}$ moiety for the iron-porphyrin complexes⁴⁵, in agreement with X-ray structure data⁴⁶. A simplified MO diagram showing the main interactions in $\text{Fe(O}_2\text{)P} \cdot \text{NH}_3$, as follows the *ab-initio* calculations⁴⁶, is presented in Figure 12.

Fig. 12. Simplified MO diagram of $\text{Fe(O}_2\text{)P} \cdot \text{NH}_3$.

One of the most recent model calculations on phthalocyanine was carried out by Sabelli et al.⁴⁰. For the di-anions of Pc and P, a procedure called CNDO-CI (Complete Neglect of Differential Overlap-Configuration Interaction) and, for the corresponding iron complexes, a method called INDO-CI (Intermediate Neglect of Differential Overlap Configuration Interaction) were employed. The calculations showed that, for FePc, both planar d orbitals (d_{xy} and $d_{x^2-y^2}$) are destabilized with respect to FeP, because it was found that the inner ring structure was smaller in the first compound. The higher negative charge on the bridge nitrogen atom of the phthalocyanine molecule compared with the corresponding bridge carbon atom of the porphyrin macrocycle also plays an important role. The result of this destabilization is an intermediate spin ($S = 1$) for the iron ion instead of the high-spin state ($S = 2$) often reported for FeP.

Sabelli et al.⁴⁰ found a very striking difference in the structures of dioxygen adducts of FePc and FeP. For the porphyrin compound, "end-on" binding of the dioxygen to the iron atom is preferred at an angle of 119° ; for the FePc model, on the other hand, the "side-on" configuration is most favourable. In the case of FePc, very little charge

Table I The structure of the dioxygen adducts of cobalt chelates^a.

Author	"en-on (bent)"	"side-on"	Co(III)-O ₂ ⁻	Co(II)-O ₂
Griffiths ⁹		+	-	-
Pauling ¹¹	+		-	-
Drago ¹⁴	+		+	
Wayland ¹⁶	+		+	
Rohmer ³⁴	+		+	
Dedieu ³⁹	+		+	
Newton ⁴²	+		+	

^a + denotes the predicted structure; - no predictions made.

transfer occurs between the iron ion and the dioxygen molecule, with almost zero net charge on the oxygen atoms. Sabelli et al.⁴⁰ also carried out a calculation with CO as a sixth ligand, to simulate the effect of a carbon support on the FeTSPc molecule. The macrocycle adsorbs on to the carbon support such that a basic group of the support may occupy the sixth coordination site. The basic group must be an electron donor, possibly an adsorbed oxygen atom or oxidized carbon and, therefore, CO is used in the calculation as an extra ligand. The result of the introduction of CO is an increase in bond energy of the dioxygen molecule by a factor of about 2. The above proposed structures for the dioxygen adducts are summarized in Tables I and II.

Dioxygen-bridged metal complexes

Dioxygen-bridged phthalocyanine dimers most likely play an important role in the reduction mechanism of the dioxygen molecule. This is discussed in detail by Elzing⁴⁷. The electronic structure of such complexes will now be discussed here. Little attention has yet been paid to theoretical considerations of dioxygen-bridged metal complexes. According to the increased-valence theory, breaking of the dioxygen bond occurs only with FeP and not with CoP, in agreement with experiments. The cleavage of this bond is often deduced from the fact that, in a dioxygen-saturated solution of FeP (but also of FePc), oxo-bridged dimers (PcFe-O-FePc) are present⁴⁸. Ochiai⁴⁹ has attempted to explain these observations by using more standard quantum-chemical concepts. He argued that the dioxygen bond splitting would present a high potential barrier when going from the dioxygen- to the oxygen-bridged dimer. The probable transition state species M⁺O⁻ (or MO) should facilitate bond cleavage. In an

energy diagram for octahedral coordination of the metal ion (Figure 13), he visualized the interactions between the *dπ* electrons on M⁺ and the odd electron on O⁻. Other interactions, such as the important σ-bonding interactions, are omitted. For a metal ion, such as iron with a *d*⁵ configuration for the iron(III) state, all low-lying levels are just occu-

Fig. 13. Energy-level diagram scheme for the transition state species M⁺O⁻.

pied and the M⁺O⁻ species is stabilized. For cobalt, the extra electron must occupy the anti-bonding orbital (ψ_2), thus no stabilization of the system is expected. The electronic structures of a cobalt μ -peroxo complex [(NH₃)₅Co-O₂-Co(NH₃)₅]⁴⁺ or a cobalt μ -superoxo complex [(NH₃)₅Co-O₂-Co(NH₃)₅]⁵⁺ have been analyzed by Vlcek⁵⁰ and Hyla-Kryspin et al.⁵¹. Vlcek assumed a structure with the dioxygen axis perpendicular to the cobalt-cobalt axis; however, a recent X-ray analysis⁵² revealed a structure for the complex with the oxygen-oxygen axis, not perpendicular, but nearing parallelism to the cobalt-cobalt axis. Hyla-Kryspin et al.⁵¹ applied the self-consistent charge and configuration molecular-orbital method to explain,

Table II The structure of the dioxygen adducts of iron chelates^a.

Author	"end-on (bent)"	"side-on"	Fe(III)-O ₂ ⁻	Fe(II)-O ₂
Griffiths ⁹		+	-	-
Pauling ^{11,12}	+		-	-
Weiss ¹³	-	-	+	
Wayland ¹⁶	+			+
Zerner ³¹		+		+
Dedieu ³⁹	+			+
Kirchner ⁴³	+			+
Case ⁴⁴	+			+
Olafson ^{45b}	+			+
Boca ⁴⁶	+			+
Sabelli ⁴⁰ FeP	+			+
Sabelli ⁴⁰ FePc		+		+

^a + denotes the predicted structure; - no predictions made.

qualitatively, some of the properties of binuclear cobalt complexes. Because of the complexity of the electronic structure, it is not easy to draw an energy-level diagram in which the interactions can be visualized. The unpaired electron, responsible for the observed paramagnetism of the μ -superoxo cobalt complex, occupies a molecular orbital containing mainly oxygen atomic orbitals. This orbital is anti-bonding and lies between the practically non-bonding $d\pi$ (d_{xy} , d_{yz} , d_{xz}) and the anti-bonding $d\sigma$ (d_{z^2} , $d_{x^2-y^2}$) orbitals of the cobalt ions. When in an energy level scheme only the molecular orbitals containing mainly oxygen atomic orbitals are depicted, a scheme of a dioxygen molecule results with an extra electron in an anti-bonding orbital: i.e., a superoxo (O_2^-) group.

When the complex is reduced, an extra electron is added to the complex and the cobalt ion will remain in the +3 oxidation state, while the superoxo (O_2^-) group is reduced to the peroxo (O_2^{2-}) group. The additional electron is also placed in an anti-bonding orbital and, therefore, the former (unreduced) complex is more stable than the latter complex. Although, Vlcek proposed a different geometry, he also concluded that the reduced complex has an additional electron in an anti-bonding orbital.

Concluding remarks

It should be noted that it is difficult to predict the reduction pathway of dioxygen based only on structural information on adsorption of the molecule on to a catalyst. In Tables I and II, it can be seen that no total consensus exists, even about the adsorption structures. This also hampers explanation of the different reduction pathways observed for CoPc and FePc on the basis of differences between the structures of their dioxygen adducts.

However, most models for dioxygen adducts of CoPc and FePc result in an "end-on" adsorption. It is, therefore, very likely that geometrical structure does not determine the reduction pathway (water or hydrogen peroxide as the end product). Most adsorption models predict that, despite the more positive redox potential of the Co^{3+}/Co^{2+} couple than that for the Fe^{3+}/Fe^{2+} couple in the phthalocyanine complex, the oxygen fragment is more negatively charged with Co than with Fe. Thus, for CoPc a hydrogen-peroxide-like species is present directly after the adsorption process, and the hydrogen peroxide pathway is likely. For FePc, cleavage of the oxygen-oxygen bond may occur before reduction, and hydrogen peroxide formation is circumvented in this way.

For dioxygen-bridged dimers of CoPc and FePc, cleavage of the oxygen-oxygen bond will occur more easily in the FePc dimer than in the CoPc dimer, because the two fragments are energetically more favourable than the corresponding ones for the CoPc dimer. Since bridged adsorption often occurs (or can occur) in systems where dioxygen is reduced to water, we expect that dioxygen-bridged phthalocyanine dimers are crucial in the reduction mechanism of dioxygen. This implies that more work is needed on the electronic structure of these dimers to elucidate the dioxygen reduction mechanism in MePc complexes.

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