Cite this: DOI: 10.1039/xxxxxxxxxx

The Dioxygen Adducts of Iron and Manganese Porphyrins: Electronic Structure and Binding Energy[†]

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Received Date

Accepted Date

DOI: 10.1039/xxxxxxxxxx

www.rsc.org/journalname

In this paper, we present a thorough study of the electronic structures and binding energies of O₂ to iron and manganese porphyrins (FeP and MnP), employing a state-of-the-art computational technique known as second-order perturbation theory based on density matrix renormalization group (DMRG-CASPT2). By investigating an extensive list of different binding modes and spin states, we provide a clear and conclusive description of the ground state of MnP–O₂, confirming available experimental evidences. Our results show that MnP–O₂ favours a side-on quartet structure, with strong charge transfer between MnP and O₂. We also calculated the standard binding enthalpies of O₂ to different metal porphyrins and showed that an agreement between calculated results and experimental data to within 2 kcal mol^{−1} can be achieved. Our calculations confirm the experimental observation that the binding of O₂ to manganese porphyrin is stronger by around 4–6 kcal mol^{−1} than to the corresponding ferrous porphyrin.

1 Introduction

Binding of O₂ to transition metal (TM) porphyrins not only plays a crucial role in many biological and biomimetic processes but also in recent developments of non-precious metal catalysts in oxygen reduction reaction (ORR).^{1–4} The heme cofactor of hemoglobin consists of an Fe ion covalently bound to a porphyrin (P). This protein can reversibly bind, carry, and release O₂ to every living cell. On the other hand, in an ORR the affinity of the metal centre to O₂ is stronger, such that it partly activates the dissociation of the O–O bond.² The ability of metal porphyrins to flexibly carry and activate O₂ is intrinsically related to the capability of the metal centre, Mn and Fe in particular, to possess different spin states and to change their oxidation state during the O₂ binding process.⁵ Both phenomena, spin state energetics and charge transfer, are notoriously difficult to describe both by density functional theory (DFT) and traditional wave function

methods (WFT). Therefore, describing the binding of O₂ to metal porphyrins is a challenging computational problem.

Over the years, the binding of O₂ to ferrous porphyrin (FeP) has already been extensively investigated in numerous studies using different theoretical methods.^{6–14} One of the most complete computational studies was performed by Radoń and Pierloot⁸ in 2008, using different DFT functionals (PBE0, B3LYP, OLYP, and BP86) as well as a more accurate *ab initio* method based on multiconfigurational perturbation theory (CASPT2).¹⁵ The authors showed that obtaining accurate binding energies of O₂ to hemes is a challenging task, requiring sizeable basis sets and rigorous correlation methods. It was shown that different DFT functionals can give very different FeP–O₂ binding energies depending on the amount of exact exchange and on whether additional corrections for spin contamination⁸ and dispersion¹⁶ are included. On the other hand, CASPT2 reproduced (at that time only available) ‘experimental data’ (10.1 kcal mol^{−1}), which was based on the O₂ dissociation barrier in myoglobin with a correction for the absence of the protein environment. More recently, it turned out that this prediction from CASPT2 is in fact very close to the experimental gas-phase measurement of $\Delta H_b^0 = 9.75 \pm 0.33$ kcal mol^{−1} for [Fe^{II}(tpps)]^{4−}–O₂ with tpps=tetrakis(4-sulfonatophenyl)porphyrin.

The binding of O₂ to Mn^{II}N₄ complexes, in particular Mn^{II} porphyrin (MnP), has so far not been well studied theoretically. MnN₄ complexes could serve as a catalyst for the four-electron ORR,² where the key step is the binding (or absorption) of O₂ to the reactive metal centre. Surprisingly, the electronic structure of MnN₄–O₂ adducts in general and MnP–O₂ in particular is

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[†] Electronic Supplementary Information (ESI) available: Electronic configurations of all investigated states. Active orbitals of MP–O₂, MP, and O₂. Schematic representation for the dissociation curves of the ground state ⁴B₂ and excited state ⁴B₁ of MnP–O₂. Structural parameters *d*(O–O) and *d*(Mn–O) of investigated states. Correlation between *d*(O–O) and *d*(Mn–O) in end-on and side-on configurations. Binding energies of O₂ to metal porphyrins calculated with DFT and DMRG-CASPT2. 3s3p correlation contributions Δ_{sp} to the binding energies, calculated with RCCSD, RCCSD(T), and CC-CR(2,3). 3s3p correlation contributions Δ_{sp} to the ionization energies of Fe²⁺ and Mn²⁺, calculated with RCCSD(T) and CASPT2. NPA charges of the metal atom in FeP, MnP, [Fe(tpps)]^{4−}, [Mn(tpps)]^{4−}, and [FehemeH]⁺. Cartesian coordinates of the ground states of FeP, FeP–O₂, MnP, and MnP–O₂. See DOI: 10.1039/b000000x/

still unclear, even though this adduct has been experimentally investigated for a long time. Several O_2 adducts of manganese(II) porphyrins ($\text{MnP}-\text{O}_2$) were synthesized and characterized around forty years ago by Basolo *et al.*^{17–19} From the results of an optical and electron paramagnetic resonance (EPR) study,¹⁷ it was concluded that $\text{MnP}-\text{O}_2$ has a quartet ground state (GS). The authors also suggested a symmetric, side-on coordination of O_2 to MnP (where O_2 is parallel to the porphyrin ring), and the $\text{Mn}^{\text{IV}}(\text{O}_2^{2-})$ formulation for the adduct. The side-on geometry was later confirmed by an infrared spectra study of the O_2 adduct of (tetraphenylporphyrinato)manganese(II) ($\text{Mn}(\text{TPP})$) in argon matrices.¹⁹ The authors further predicted a strong charge-transfer from MnP to O_2 , leading to a negative charge on O_2 somewhere between O_2^- (superoxide) and O_2^{2-} (peroxide). Recently, Gallagher *et al.*²⁰ for the first time successfully isolated and provided crystallographic and spectroscopic characterization of a four-coordinate manganese(II) porphyrin centre and its corresponding O_2 adduct in a metal–organic framework (MOF). Using single-crystal X-ray diffraction and EPR analyses, the authors showed that $\text{MnP}-\text{O}_2$ can be described as a peroxo ligand bound in a side-on mode to a quartet Mn^{IV} ion. Furthermore, the authors measured an O_2 adsorption enthalpy of $\sim 12 \text{ kcal mol}^{-1}$. This value is slightly smaller than gas-phase experimental value of $[\text{Mn}^{\text{II}}(\text{tpps})]^{4-}$ ($\sim 16 \text{ kcal mol}^{-1}$) recently reported by Karpuschkin *et al.*²¹

Theoretical studies on $\text{MnP}-\text{O}_2$ are expected to complement the experimental results, e.g. by providing insights into the electronic structure of the GS or by quantitatively evaluating the binding energy of O_2 to the metal centre. However, the results of previous theoretical studies quite often conflicted with experimental observations.^{17,19} To the best of our knowledge, theoretical studies on $\text{MnP}-\text{O}_2$ have only been performed with DFT and single-reference wave function methods, except a very recent work of Kappes *et al.*²² The earliest work was done by Dedieu and Rohmer,²³ in which the authors employed Hartree-Fock to study 14 probable electronic configurations of both side-on (Griffiths model) and end-on (Pauling model) geometries (Figure 1). The authors found a end-on GS corresponding to $\text{Mn}^{\text{III}}(\text{O}_2^-)$, in contradiction to the experiments. Newton and Hall²⁴ later studied this adduct using configuration interaction (CI) and predicted a quartet side-on GS. However, because of the high uncertainty in the theoretical approach, the authors could not eliminate the possibility of a end-on GS. Much later, Cramer *et al.*²⁵ employed DFT to study a series of metal- O_2 adducts including $\text{MnP}-\text{O}_2$. The authors correctly calculated the side-on quartet GS of $\text{MnP}-\text{O}_2$, however, no other excited states were calculated and the electronic structures were not provided. Since 2005, quite some DFT studies^{26–30} on Mn- O_2 adducts have been presented, but all of them, up to a certain point, disagreed with either the experimental data of Basolo *et al.*,^{17–19} or recent results of Karpuschkin *et al.*²¹ and Gallagher *et al.*²⁰ Calculations employing hybrid functionals point to vastly different electronic structures of the GS: sextet side-on in the works of Kasai *et al.*^{26,27} and Costa *et al.*,³⁰ doublet side-on presented by Flyagina *et al.*²⁹, or even end-on configuration.²⁸ In some of these works,^{28,30} the binding energies of O_2 to manganese porphyrins were also

Fig. 1 Different binding modes of the $\text{MP}-\text{O}_2$ adduct: end-on (C_s) and side-on (C_{2v}). (a): the O–O bond bisects the N–Fe–N angle and (b): the O–O bond eclipses one of the Fe–N bonds.

estimated, however, the calculated binding energies were usually too low by $\sim 4\text{--}6 \text{ kcal mol}^{-1}$ as compared to the gas phase data.²¹

During preparation of this manuscript a report by Kappes *et al.*²² was published, studying the electronic structures and binding energies of $\text{MP}-\text{O}_2$ ($M = \text{Fe}, \text{Mn}$) using CASPT2. Employing very limited and unbalanced active spaces, as well as small basis sets, the authors found a quartet GS for MnP and a quartet end-on GS for $\text{MnP}-\text{O}_2$. Both findings are in contradiction to either previous experiments or high-quality theoretical calculations: MnP ground state is a sextet,^{17,18,20,31–33} and $\text{MnP}-\text{O}_2$ should have a side-on configuration.²⁰ Needless to say that the excellent agreement between the calculated and experimental data (within 1 kJ mol^{-1}) in the work of Kappes *et al.* comes from fortuitous error cancellations between *wrong* ground states and low-level wave function calculations.

Given the controversy on this matter, the first goal of this work is to provide a clear assignment of the GS electronic structure of $\text{MnP}-\text{O}_2$. We employ a state-of-the-art multireference technique, known as perturbation theory^{34–37} based on density matrix renormalization group^{38–46} (DMRG-CASPT2), in order to study various electronic states of $\text{MnP}-\text{O}_2$ and to search for the GS. Motivated by the successful prediction of CASPT2 for the binding energy of $\text{FeP}-\text{O}_2$,⁸ we further calculate the binding energies of O_2 to both MnP and FeP. The calculated results will be compared with recent gas-phase experimental data by Karpuschkin *et al.*²¹ for $[\text{Fe}^{\text{II}}(\text{tpps})]^{4-}$ and $[\text{Mn}^{\text{II}}(\text{tpps})]^{4-}$ and Shafizadeh *et al.*⁴⁷ for protonated ferrous heme⁴⁸ $[\text{Fe}^{\text{II}}\text{hemeH}]^+$ (see Figure 2).

2 Computational Details

All geometries were obtained using the BP86 functional^{49,50} implemented in TURBOMOLE v.7.0.⁵¹ Stuttgart effective-core potentials (ECP) and the associated basis set ECP-10-MDF⁵² were used for the metal atom, while the 6-31G(d) basis set was employed for the ligand atoms. For $\text{FeP}-\text{O}_2$, the structure is the same as used before in the work of Radoń and Pierloot.⁸ The Cartesian coordinates of the GS structures can be found in the Supplementary Information.

In $\text{FeP}-\text{O}_2$, the electronic structure of the singlet GS is well-defined.^{6–8} Therefore, we only studied the lowest singlet state of two end-on structures: C_s (a) (the O–O bond bisects the N–Fe–N angle) and C_s (b) (the O–O bond eclipses one of the Fe–N bonds) (Figure 1).

Since the GS electronic structure of $\text{MnP}-\text{O}_2$ is still under debate, we investigated multiple quartet states suggested by

Fig. 2 Binding of O_2 to metal porphyrins investigated by Karpuschkin *et al.*²¹ ($[\text{Fe}^{\text{II}}(\text{tpps})]^{4-}$ and $[\text{Mn}^{\text{II}}(\text{tpps})]^{4-}$) and Shafizadeh *et al.*⁴⁷ ($[\text{Fe}^{\text{II}}\text{hemeH}]^+$).

the experimental data^{17,20} as well as sextet states predicted by several theoretical studies employing hybrid functionals.^{26,30} We calculated four binding modes, shown in Figure 1: two end-on C_s (a), C_s (b); and two side-on C_{2v} (a), C_{2v} (b) structures. For each structure, multiple potentially low-lying electronic states were calculated. The states were first generated by distributing 7 valence electrons in 7 orbitals. A large portion of high-lying states, containing either empty bonding orbitals or doubly-occupied anti-bonding orbitals, were not considered. We then optimized the molecular structures of the remaining states using BP86. Some states were further discarded as the self-consistent field (SCF) failed to converge. We note that the number of sextet states is quite limited because most of them dissociate into MnP and O_2 . A list of 35 states, containing 25 quartet and 10 sextet was finally chosen. This extensive list is expected to contain *all* quartet and sextet states previously investigated.^{22–28,30} The electronic configurations of all states considered can be found in Figures S1–S5.

DMRG-CASPT2 calculations were performed on top of the MP– O_2 optimized structures in order to identify the GS and evaluate the M– O_2 binding energies. In all DMRG calculations, an extensive active space up to 21 active orbitals was employed. The active space consists of five (predominantly) metal 3d orbitals as well as two O_2 anti-bonding π_{2p}^* orbitals that can overlap the metal 3d orbitals (see also Figure 4). The two π_{2p}^* orbitals are denoted as $\pi_{\perp}^*$ (perpendicular to the porphyrin ring P) and $\pi_{\parallel}^*$ (parallel with P). In order to properly describe the elongation of the O–O bond in MP– O_2 , the active space was further augmented with five O_2 orbitals: two bonding orbitals π_{2p} , one bonding orbital σ_{2p} , and the corresponding anti-bonding orbital σ_{2p}^* . Additionally, we also included one $\sigma_{\text{M–N}}$ orbital describing the covalent interaction between the metal centre and the four N ligand atoms. Finally, to account for the so-called ‘double-shell’ effect,⁵³ the active space was further extended with two π_{3p} and two π_{3p}^* orbitals of O_2 as well as some (but not all) 4d orbitals of the metal atom. We note that only the 4d orbitals correlating to singly or doubly occupied 3d orbitals were included in the active space. For MP, we employed an active space with 11 active orbitals containing 7 and 8 electrons (denoted as CAS(7,11) and CAS(8,11)) for MnP (sextet) and FeP (triplet), respectively. This active space consists of five metal 3d orbitals,

five ‘double-shell’ metal 4d orbitals, and the $\sigma_{\text{M–N}}$ orbital. For O_2 , we employed a CAS(8,10) active space comprising two σ orbitals, four π orbitals, as well as the corresponding ‘double-shell’ π_{3p} and π_{3p}^* . The active natural orbitals of MP– O_2 , MP, and O_2 can be found in Figures S6–S9.

In all DMRG calculations, we used two families of basis sets. The first, denoted as BS1, consists of relativistic natural orbital (ANO-RCC) type basis sets. The contractions are [7s6p5d3f2g1h] for the metal atom;⁵⁴ [4s3p2d1f] for O, C, and N;⁵⁵ and [3s1p] for H.⁵⁶ This basis set was employed to study the relative energies between different electronic states in the MP– O_2 adducts. To obtain accurate binding energies, we used a significantly larger correlation consistent (cc-) basis sets: aug-cc-pwCVnZ-DK ($n = 4, 5$) for the metal atom;⁵⁷ aug-cc-pVQZ-DK for O, C, and N;⁵⁸ and cc-pVQZ-DK for H.⁵⁹ The results were extrapolated to complete basis set (CBS) limit using the two-point extrapolation formula of Helgaker *et al.*⁶⁰ The cost of the calculations was reduced using the Cholesky decomposition technique for the two electron integrals⁶¹ with a threshold of 10^{-6} au. Scalar relativistic effects were included using a standard second-order Douglas-Kroll-Hess (DKH) Hamiltonian.^{62–64}

All DMRG calculations were done with the spin-adapted DMRG algorithm, implemented in the CHEMPS2 code,⁶⁵ interfaced with MOLCAS v.8.3.⁶⁶ The number of renormalized states is $m = 2000$, which should give converged DMRG-CASPT2 relative energies to within 1 kcal mol^{−1} for medium-sized active spaces (around 20–24 active orbitals).³⁷ The orbital ordering was automated by minimizing the quantum entanglement using Fiedler ordering.⁶⁷ A perturbative noise (noise prefactor of 0.05) was added into the wave function in the warm-up sweep to prevent the DMRG algorithm from being trapped at a local minimum. We used a residual norm threshold 10^{-7} for the Davidson algorithm in the last sweep. In the last iteration of DMRG-CASSCF, the optimized natural orbitals were canonicalized. In this way, the pseudocanonical Fock matrix contracted with the four-body reduced density matrix (4-RDM) can be efficiently calculated and we can avoid the computation of the expensive full 4-RDM.³⁴ This strategy works well for compact or highly symmetric molecules.³⁶

In all PT2 calculations, we used the standard ionization potential electron affinity (IPEA) shift of 0.25 au.⁶⁸ An imaginary

shift⁶⁹ of 0.1 au was applied in order to prevent weak intruder states and improve convergence. All valence electrons of the ligand atoms were correlated. Recently, we have shown that CASPT2 has difficulties describing correlation of the semicore electrons (3s and 3p electrons) of the metal atom.^{33,70} Hence, we reported the relative energies between different states *without* these eight electrons in the PT2 treatment.

Knowing the GS of FeP–O₂ and MnP–O₂, we further investigated the nature of the M–O₂ bond. This can be done by analysing the DMRG natural orbital occupation numbers (NOONs) as well as the dominant Slater determinants (SDs) of the wave function, calculated with a recently developed configuration interaction algorithm known as heat-bath CI (HCI).^{71,72} The diradical character of a bond *i* can be linked in a simple manner to its multiconfigurational character, manifested by the NOONs of the two (bonding and antibonding) orbitals involved in the bond⁷³:

$$Y_i = (1 - \frac{n^+ - n^-}{2}) \cdot 100\%$$

with Y_i the diradical character of the bond (in percentage), and n^+ and n^- the NOON of the bonding and antibonding molecular orbitals, respectively ($n^+ + n^- \approx 2$).

We then calculated the binding energies ΔE_{MPO_2} of O₂ from FeP–O₂ and MnP–O₂. As mentioned above, we extrapolated the metal basis set to CBS, while keeping the ligand basis set fixed at the quadruple zeta quality. At this CBS level, the basis set superposition error (BSSE) is expected to be very small. We thus decided *not* to include the counterpoise correction for BSSE in the binding energies. In a recent study⁷⁴ it was shown that counterpoise-corrected bond energies might deviate more from the basis set limit numbers than uncorrected bond energies.

As mentioned above, the 3s3p correlation contribution cannot be accurately calculated at the PT2 level³³ but this contribution (of several kcal mol^{−1}) should of course not be neglected when aiming for accurate binding energies. Therefore, we estimated the 3s3p contribution to the binding energy using a cheap (but accurate) strategy recently proposed,⁷⁰ employing coupled-cluster singles and doubles plus perturbative triples (CCSD(T)), in combination with aug-cc-pwCVTZ-DK basis set on the metal atom and minimal basis sets on the ligand atoms. Because of the more pronounced multiconfigurational character of MP–O₂ (*vide infra*), we used a coupled-cluster method that can partly handle electronic near-degeneracies, known as completely renormalized (CR) coupled-cluster (CR-CCSD(T)_g or CR-CC(2,3)).⁷⁵ The CR-CC(2,3) calculations were done with the GAMESS software.⁷⁶

Finally, we estimated the O₂ binding energies of the complexes investigated in the experiments, i.e. [M^{II}(tpps)]⁴⁺–O₂²¹ and [Fe^{II}hemeH]⁺–O₂.⁴⁷ Because these complexes are noticeably larger than our small model MP–O₂, we calculated their O₂ binding energies by simply adding a model correction to ΔE_{MPO_2} . This correction was calculated by taking the difference between the binding energies of the small and large models, using the dispersion-corrected (D3BJ)^{77,78} BP86 functional and a large def2- basis set (def2-QZVPP for the metal atom and def2-TZVP for the ligand atoms).

3 Results and Discussion

3.1 The Electronic Structure of FeP–O₂ and MnP–O₂

We first used DMRG-CASPT2/BS1 to calculate the GS of FeP–O₂ (end-on open-shell singlet)^{8,79,80} and to identify the most stable state of MnP–O₂. We shall briefly discuss the results of FeP–O₂ and focus more on the electronic structure of MnP–O₂.

3.1.1 Ground State of FeP–O₂

In FeP–O₂, we first observed that the two end-on configurations $C_s(a)$ and $C_s(b)$ are close-lying with an energy difference of only 2 kcal mol^{−1}. This small energy gap suggests that the rotational barrier between the two configurations is low, i.e. O₂ can easily rotate around the Fe–O axis. Indeed, experiments of various oxyheme complexes^{81–83} showed that both end-on configurations $C_s(a)$ and $C_s(b)$ can be observed. Here, we discuss in detail the most stable configuration $C_s(a)$ (with the O–O bond bisecting the N–Fe–N angles). The nature of the bond between FeP and O₂ will be analysed based on both the DFT structure and DMRG/HCI wave function. We note that over 80 years, the adduct of O₂ and ferrous porphyrin has been extensively investigated. While its electronic structure could be well-described using multiconfigurational methods such as CASSCF, the debate whether the ground state can be represented by a simple model such as Pauling ¹Fe^{II}–¹O₂,⁸⁴ Weiss ²Fe^{III}–²O₂,⁸⁵ or McClure-Goddard ³Fe^{II}–³O₂^{86,87} is still ongoing.^{6,7,80,88–96} The reason for this never-ending debate is that different experimental techniques⁹⁵ (infrared, Raman, Mössbauer, X-ray absorption spectroscopy, and X-ray diffraction) and theoretical methods⁶ (DFT, CASSCF, GVB, etc.) support different models. Moreover, the environment of the Fe–O₂ moiety, such as the axial ligand,⁹⁷ hydrogen bond, or solvent effect,⁶ could alter the GS electronic structure. We refer the reader to a recent excellent perspective by Bren *et al.*⁹⁵ providing a thorough picture of current understanding on the nature of the Fe–O₂ bond.

Structural parameters of FeP–O₂ calculated with BP86 (O–O, Fe–O bond lengths, and O–O vibrational frequency) are shown in the first column of Table 1. The calculated results can be compared with experimental data of 5-coordinate heme–O₂ complexes: infrared spectra of FeTPP–O₂ in Ar matrix^{89,98} and an X-ray diffraction of heme containing MOF (PCN-224)Fe–O₂.⁹⁷ To the best of our knowledge, (PCN-224)Fe–O₂ is the first and only “base-free” heme–O₂ complex that has been structurally characterized. Unfortunately, because of the crystallographic disorder of O₂, the reported values in (PCN-224)Fe–O₂, especially the O–O bond distance, might have large uncertainties. Indeed, the measured $d(\text{O–O})$ is unrealistically short (1.15 ± 0.04 Å), even smaller than the O–O bond distance in an isolated O₂ (1.21 Å). We thus observed a large discrepancy of more than 0.1 Å between the X-ray $d(\text{O–O})$ and the DFT value. We note that a similar discrepancy has been found in previous theoretical studies on 6-coordinate heme–O₂ complexes.¹⁴

On the other hand, other DFT data are in fair agreement with the experimental values: the Fe–O bond distance is overestimated by 0.02 Å and the vibrational frequency $\nu(\text{O–O})$ is overestimated

Table 1 Structural parameters of MP–O₂ calculated with BP86 and diradical character of the M–O₂ bond calculated with DMRG

	FeP–O ₂ ¹ A' C _s (a)		MnP–O ₂ ⁴ B ₂ C _{2v} (b)		O ₂
	BP86	Exp.	BP86	Exp.	
<i>d</i> (O–O) (Å)	1.279	1.15 ± 0.04 ^a	1.381	1.40 ± 0.02 ^b	1.208
<i>d</i> (M–O) (Å)	1.810	1.79 ± 0.01 ^a	1.858	1.76 ± 0.03 ^b	
<i>v</i> (O–O) (cm ^{−1})	1242.2	1106–1223 ^c	1022.7	983 ^d	1580.2
<i>Y</i> (%)	46				
<i>Y</i> _⊥ (%)	22		26		

^a Ref. 97, measured in (PCN-224)Fe–O₂. ^b Ref. 20, measured in (PCN-224)Mn–O₂. ^c Ref. 89,98, measured in FeTPP–O₂. ^d Ref. 19, measured in MnTPP–O₂.

by 19–136 cm^{−1}. Both DFT and IR spectroscopy show that the vibrational frequency *v*(O–O) in FeP–O₂ is strongly reduced as compared to molecular oxygen. The O–O group in a complex may be classified based on the criteria of Cramer *et al.*²⁵: peroxides have a *d*(O–O) of ~1.4–1.5 Å and *v*(O–O) between 800 and 930 cm^{−1}, whereas compounds with *d*(O–O) ≈ 1.2–1.3 Å and *v*(O–O) ≈ 1050–1200 cm^{−1} are superoxides. The DFT results (*d*(O–O) = 1.28 Å and *v*(O–O) = 1242 cm^{−1}) thus suggest that FeP–O₂ could be described as a superoxide O₂[−] coordinated to a ferric iron centre (²Fe^{III}–²O₂[−]).

We now turn our attention to the GS wave function calculated with DMRG and HCI. The HCI wave function can be qualitatively described as a combination of two SDs (representing 76% of the total wave function): $\Psi = 0.792 | \dots (d_{xz} + \pi_{||}^*)^2 (d_{xz} - \pi_{||}^*)^0 | - 0.369 | \dots (d_{xz} + \pi_{||}^*)^0 (d_{xz} - \pi_{||}^*)^2 |$, where $(d_{xz} + \pi_{||}^*)$ and $(d_{xz} - \pi_{||}^*)$ are the bonding and anti-bonding combinations between *d*_{xz} and $\pi_{||}^*$, respectively ($\pi_{||}^*$ denoting the O₂ π^* orbital oriented parallel to the FeP plane, see also Figure 4). The wave function has a considerable multiconfigurational character and is in qualitative agreement with previous CASSCF results employing smaller active spaces.^{6–8} The multiconfigurational nature is also represented by large deviations of the DMRG NOONs from the ‘single reference’ values (either two or zero). The NOONs of $(d_{xz} + \pi_{||}^*)$ and $(d_{xz} - \pi_{||}^*)$ are 1.56 and 0.48, respectively. This translates into a considerable diradical character *Y*_{||} of 46%, showing that approximately, each magnetic orbital Fe *d*_{xz} and O₂ $\pi_{||}^*$ holds one electron. On the other hand, (with $\pi_{\perp}^*$ denoting the O₂ π^* orbital oriented perpendicular to the FeP plane) the NOONs of $(d_{z^2} + \pi_{\perp}^*)$ and $(d_{z^2} - \pi_{\perp}^*)$ are 1.79 and 0.23, respectively, showing a smaller, but non-negligible diradical character *Y*_⊥ of 22%. Based on the diradical character of the Fe–O₂ bond, we agree with Solomon *et al.*⁹¹ that the electronic structure of this highly multiconfigurational complex cannot be exclusively described by either the Pauling, Weiss, or McClure-Goddard model. We assign the wave function of FeP–O₂ in the gas-phase as the Weiss ²Fe^{III}–²O₂[−] configuration, with a non-negligible contribution of the McClure-Goddard ³Fe^{II}–³O₂ structure. Our assignment is supported by recent X-ray absorption spectroscopy studies on oxyhemoglobin and oxymyoglobin in solutions.^{92,94,96} These studies recommended either Weiss or McClure-Goddard

structures, implying the multiconfigurational description of heme–O₂ complexes.

3.1.2 Ground State of MnP–O₂

As mentioned above, an extensive list of states, including 25 quartet and 10 sextet states, was calculated. The electronic configurations of all states are shown in Figures S2–S5. Most importantly, DMRG-CASPT2/BS1 confirms the experimental evidence that MnP–O₂ has a quartet GS and that O₂ binds to Mn in a side-on manner, with the O–O bond eclipsing the pyrrole-based N atoms (⁴B₂ C_{2v}(b)).^{17,19,20}

The structural parameters of the GS are shown in Table 1. The results are in close agreement with previous DFT data reported by Cramer *et al.*²⁵ (*d*(O–O) = 1.377 Å and *v*(O–O) = 1009 cm^{−1}). Our calculated vibrational frequency *v*(O–O) also agrees well with the experimental value¹⁹ (within 40 cm^{−1}). Less good agreement is found between the gas-phase DFT structure and the crystal structure of (PCN-224)Mn–O₂:²⁰ BP86 predicts a larger *d*(O–O) by ~0.02 Å, and yields a considerably larger *d*(Mn–O) by almost 0.1 Å. We again attribute this disagreement to crystallographic disorder of O₂ in the experiments of Gallagher *et al.*²⁰

In comparison with both FeP–O₂ and molecular oxygen, the O–O bond in MnP–O₂ is notably weaker, i.e. it has a larger *d*(O–O) and smaller *v*(O–O). On the basis of the criteria of Cramer *et al.*²⁵ (see above), the O₂ moiety in MnP–O₂ could be designated as a mixture of peroxide and superoxide.

A qualitative picture of the bonding between between ⁶Mn^{II}P and ³O₂ in the ⁴B₂ GS is provided by the molecular orbital (MO) diagram in Figure 3, displaying the interactions between the two O₂ π^* and five metal 3d orbitals. The Figure also includes the DMRG natural orbitals and their corresponding NOONs. We note that this MO diagram can also be used for a qualitative description of other (excited) states with a side-on structure (see next section). Due to symmetry restrictions the O₂ $\pi_{\perp}^*$ and $\pi_{||}^*$ orbitals can only interact with *d*_{xz} and *d*_{xy}, respectively. The former interaction is clearly the stronger one, as it leads to a covalent π bond. In contrast, the *d*_{xy}– $\pi_{||}^*$ interaction forms a significantly weaker δ bond. Because of this weak interaction, the bonding orbital is predominantly $\pi_{||}^*$, whereas the antibonding orbital is mainly *d*_{xy}. The *d*_{x²−y²} orbital interacts with the nitrogen lone pairs of the porphyrin system, forming a

high-lying antibonding orbital. Finally, the other metal orbitals d_{z^2} and d_{yz} remain pure metal 3d since they only negligibly interact with the O_2 π orbitals. Based on the MO diagram, the electronic configuration of the quartet GS can be written as $(d_{xz} + \pi_{\perp}^*)^2(d_{xy} + \pi_{\parallel}^*)^2(d_{xy} - \pi_{\parallel}^*)^{\uparrow}(d_{z^2})^{\uparrow}(d_{yz})^{\uparrow}$.

An HCI analysis shows that the GS can essentially be described as a combination of two SDs, representing 79% of the total wave function: $\Psi = 0.857|\dots(d_{xz} + \pi_{\perp}^*)^2(d_{xz} - \pi_{\perp}^*)^0| - 0.231|\dots(d_{xz} + \pi_{\perp}^*)^0(d_{xz} - \pi_{\perp}^*)^2|$. Undoubtedly, the multiconfigurational character of the wave function mainly originates from the strong correlation between the bonding and antibonding combinations of Mn d_{xz} and O_2 $\pi_{\perp}^*$. The NOONs of $(d_{xz} + \pi_{\perp}^*)$ and $(d_{xz} - \pi_{\perp}^*)$ orbitals are 1.75 and 0.27, respectively. This corresponds to a diradical character $Y_{\perp}$ of 26%, small but not insignificant. However, in comparison with FeP- O_2 (discussed in the previous section), the GS wave function of MnP- O_2 is considerably less diradical, i.e. the total diradical character in MnP- O_2 is only 26%, much less than the combination of $Y_{\perp}$ (22%) and $Y_{\parallel}$ (46%) in FeP- O_2 . The smaller diradical character of MnP- O_2 also means that the metal and O_2 oxidation states remain much closer to their formal values, Mn^{IV} and O_2^{2-} , than in FeP- O_2 . Hence, MnP- O_2 can be qualitatively described as a mixture of two models: minor $^3\text{Mn}^{\text{III}}-^2\text{O}_2^-$ and major $^4\text{Mn}^{\text{IV}}-^1\text{O}_2^{2-}$. We agree with the very early prediction of Basolo *et al.*^{17,19} that O_2 is somewhere between O_2^- and O_2^{2-} .

Knowing the GS electronic structure, it is also interesting to understand the binding mechanism between O_2 and MnP. We propose a mechanism with two different oxidation processes: a “slow” one associated with the interaction between d_{xz} and $\pi_{\perp}^*$ orbitals; and a “fast” one involving a crossing between the potential energy surfaces of two states. The former oxidation process is called “slow” in the sense that it occurs along the reaction pathway. At large Mn–O distance, the electronic configuration of MnP- O_2 is $(d_{xy})^{\uparrow}(d_{z^2})^{\uparrow}(d_{yz})^{\uparrow}(d_{x^2-y^2})^{\uparrow}(d_{xz})^{\uparrow}(\pi_{\perp}^*)^{\downarrow}(\pi_{\parallel}^*)^{\downarrow}$, giving rise to a $^4\text{B}_1$ state (the combination of $^6\text{A}_1$ on MnP and $^3\text{B}_1$ on O_2). As the Mn–O distance decreases, d_{xz} and $\pi_{\perp}^*$ start to overlap and gradually mix into a bonding $(d_{xz} + \pi_{\perp}^*)$ (still predominantly O_2) and antibonding $(d_{xz} - \pi_{\perp}^*)$ (still predominantly Mn 3d) combination, where the former increases its occupation number towards two at the expense of the latter, such that Mn is gradually oxidized. On the other hand, the “fast” oxidation process occurs at a crossing point between two potential energy surfaces, known as minimum energy crossing point (MECP).⁷⁹ In order to reach the $^4\text{B}_2$ ground state, the complex must cross from $^4\text{B}_1$ to $^4\text{B}_2$ through an MECP. This is accomplished by an electron transfer from Mn $d_{x^2-y^2}$ into O_2 $\pi_{\parallel}^*$. Therefore, around the MECP, Mn is ‘suddenly’ oxidized. We attempted to locate the MECP and determine whether an energy barrier might exist between the two potential energy surfaces of $^4\text{B}_2$ and $^4\text{B}_1$. Such calculation is not possible at the DMRG-CASPT2 level of theory because analytical gradients are not available. Instead, we located the MECP using DFT (B97-D/def2-TZVP, see Figure S10) but found no reaction barrier between the two potential energy surfaces at this level.

3.1.3 Excited States of MnP- O_2

The structural parameters ($d(\text{O}-\text{O})$ and $d(\text{Mn}-\text{O})$) of all states can be found in Figures S11 and S12. In general, we can only find a weak inverse-correlation between $d(\text{O}-\text{O})$ and $d(\text{Mn}-\text{O})$: long O–O bond distance associates with short Mn–O bond length. This can be rationalized by the fact that a shorter $d(\text{Mn}-\text{O})$ causes a stronger overlap between the metal 3d and O_2 π^* orbitals, a decrease of the diradical character, and an increase of the electron population of O_2 π^* . This inverse-correlation has been observed and explained for the GS of metal- O_2 complexes in a previous work of Cramer *et al.*²⁵ In contrast, we could not identify any correlation between the structural parameters and the relative energies.

The electronic configurations and excitation energies of all excited states are presented in Figures S2–S5. All 24 quartet and 10 sextet excited states are higher in energy than the GS by at least ~ 8 kcal mol^{−1}. Here, we do not attempt to describe all excited states but only discuss the lowest state of each binding mode: $^4\text{A}''$ of $C_s(\text{a})$ and $C_s(\text{b})$, $^6\text{A}_1$ $C_{2v}(\text{a})$, and the GS $^4\text{B}_2$ $C_{2v}(\text{b})$. In Figure 4, we show the electronic structures (electronic configuration, DMRG natural orbitals, and NOONs) of these four states. For convenience, the coordinate axes were chosen so that the metal d_{xz} always overlaps with one of the O π^* orbitals, whereas d_{yz} is always non-bonding.

The binding of O_2 and MnP in the two end-on configurations $^4\text{A}''$ can be described by two bonds: a strong σ bond arising from the interaction between d_{z^2} and $\pi_{\perp}^*$ and a weaker π bond resulting from the $d_{xz}-\pi_{\parallel}^*$ interaction. A closer look at the electronic structure of these two end-on configurations reveals that they are closely related: the two bonding orbitals $(d_{z^2} + \pi_{\perp}^*)$ and $(d_{xz} + \pi_{\parallel}^*)$ are doubly occupied, while the three (predominantly) metal 3d orbitals are singly occupied. Consequently, the relative energy between these two states is small (less than 0.5 kcal mol^{−1}). This again suggests that rotation between the two end-on configurations should be easy. We finally note that, as compared to the GS of MnP- O_2 , both end-on configurations exhibit a stronger multiconfigurational character with a significantly larger diradical character ($Y_{\parallel} = 70 - 80\%$ and $Y_{\perp} = 50 - 60\%$).

Considering the similarity between the two end-on configurations, one might expect a state in $C_{2v}(\text{a})$ that is energetically close-lying to the GS $^4\text{B}_2$ $C_{2v}(\text{b})$. However, the lowest quartet state $^4\text{B}_1$ (with principal configuration $(d_{xz} + \pi_{\perp}^*)^2(\pi_{\parallel}^*)^2(d_{x^2-y^2})^{\uparrow}(d_{z^2})^{\uparrow}(d_{yz})^{\uparrow}$) is high-lying (+13.3 kcal mol^{−1}, see Figure S4). That this state, with a similar configuration as the $^4\text{B}_2$ GS, is considerably higher in energy might be brought back the presence of a strongly diradical δ -interaction between $\pi_{\parallel}^*$ and d_{xy} . This interaction gives rise to a large population (~ 0.7) of the latter orbital, which is also σ -antibonding with the P N-ligands. In fact it turns out that the lowest $C_{2v}(\text{a})$ state is a sextet state ($^6\text{A}_1$). This state, where the antibonding orbital $(d_{xz} - \pi_{\perp}^*)$ becomes populated, is ~ 9 kcal mol^{−1} higher in energy than the GS.

Fig. 3 Molecular orbital diagram of the ⁴B₂ ground state of MnP–O₂. The orbitals are DMRG natural orbitals and the blue numbers represent the corresponding NOONs.

Fig. 4 Electronic configuration of the lowest state of each binding mode. The orbitals are DMRG natural orbitals and the blue numbers represent the corresponding NOONs.

Table 2 Calculated standard binding enthalpy $\Delta H_{\text{MPO}_2}^\circ$ (in kcal mol⁻¹) of O₂ to MP (M = Fe, Mn)

	FeP–O ₂	MnP–O ₂
$\Delta E(\text{PT2})^a$	13.4	11.2
Δ_{sp}^b	–4.3	2.5
ZPE ^c	–1.0	–2.8
Thermal correction ^c	0.2	1.0
$\Delta H_{\text{MPO}_2}^\circ$	8.3	11.9

^a $\Delta E(\text{PT2}) = E_{\text{MP}} + E_{\text{O}_2} - E_{\text{MP-O}_2}$. ^b 3s3p correlation correction calculated at CR-CC(2,3) level (BSSE included).

^c ZPE and thermal corrections calculated with BP86.

3.2 Standard Binding Enthalpies of O₂ to Metal Porphyrins

3.2.1 Standard Binding Enthalpies of O₂ to FeP and MnP

In this section we calculate the standard binding enthalpy of O₂ to MP ($\Delta H_{\text{MPO}_2}^\circ$) corresponding to the reaction $\text{MP-O}_2 \longrightarrow \text{MP} + \text{O}_2$. The results are presented in Table 2. $\Delta H_{\text{MPO}_2}^\circ$ consists of three components: the DMRG-CASPT2 binding energy $\Delta E(\text{PT2}) = E_{\text{MP}} + E_{\text{O}_2} - E_{\text{MP-O}_2}$, the 3s3p correlation correction Δ_{sp} calculated at CR-CC(2,3) level of theory, and the ZPE and thermal corrections calculated with BP86.

As can be seen in Table 2, without the 3s3p correlation correction, DMRG-CASPT2 predicts similar binding energies $\Delta E(\text{PT2})$ for FeP–O₂ and MnP–O₂ (13.4 and 11.2 kcal mol⁻¹, respectively). These results contradict the experimental observation by Karpuschkin *et al.*²¹ that O₂ binds to MnP much stronger than to FeP. The contradiction is resolved after adding the 3s3p correlation correction: the binding energy in FeP–O₂ is lowered to 9.1 kcal mol⁻¹, while in MnP–O₂ it is increased to 13.7 kcal mol⁻¹. This again points to a crucial role of 3s3p correlation in calculations of relative energies of TM complexes.³³ Interestingly, 3s3p correlation behaves differently in FeP–O₂ and MnP–O₂. In FeP–O₂, it significantly weakens the Fe–O₂ bond, by 4.3 kcal mol⁻¹ whereas in MnP–O₂, it strengthens the Mn–O₂ bond by 2.5 kcal mol⁻¹. The negative number in FeP–O₂ seems to contradict a previous finding³³ that Δ_{sp} should stabilize states with a low number of unpaired 3d electrons (¹FeP–O₂) with respect to states with high number of unpaired 3d electrons (³FeP + ³O₂). However, in a redox reaction such as $^1\text{FeP-O}_2 \longrightarrow ^3\text{FeP} + ^3\text{O}_2$, the relative 3s3p correlation contribution of course does not solely depend on the spin states of the reactants and products, but also on the metal oxidation state. Indeed, a preliminary study on the ionization energies of Fe²⁺ and Mn²⁺ cations (see Table S4) indicates that the 3s3p correlation contribution tends to (strongly) stabilize lower with respect to higher oxidation states. This aspect of 3s3p correlation should therefore give a negative (bond weakening) contribution to Δ_{sp} , while the fact that metal–O₂ bond formation decreases the number of unpaired 3d electrons should give a positive (bond strengthening) contribution. The overall sign of Δ_{sp} obviously depends on the balance between these two contributions.

Finally, the standard binding enthalpy $\Delta H_{\text{MPO}_2}^\circ$ was obtained by including the ZPE and thermal corrections. They only contribute

to $\Delta H_{\text{MPO}_2}^\circ$ by –0.8 and –1.8 kcal mol⁻¹ in FeP–O₂ and MnP–O₂, respectively. The more negative corrections in MnP–O₂ are attributed to the fact that MnP–O₂ is structurally more compact than FeP–O₂, as shown in Table 1.

3.2.2 Comparison to Experiments

In order to directly compare with several sets of experimental data in the gas-phase,^{21,47} $\Delta H_{\text{MPO}_2}^\circ$ was further augmented with the model correction ΔE_{MC} . This correction accounts for the fact that a substituent at either eight β -carbons or four *meso*-carbons can alter the O₂ binding energy.^{28,47} The results are shown in Table 3. Two important trends can be seen from both theoretical and experimental results. First, O₂ always binds stronger to the Mn than to the corresponding Fe complex by 4–6 kcal mol⁻¹. The experimental data²¹ show that the O₂ binding enthalpies in $[\text{Fe}(\text{tpps})]^{4-}\text{-O}_2$ and $[\text{Mn}(\text{tpps})]^{4-}\text{-O}_2$ are 9.75 ± 0.33 and 16.10 ± 0.53 kcal mol⁻¹, respectively. Our theoretical predictions are in excellent agreement with these experiments with errors less than 2 kcal mol⁻¹.

The second trend can be seen from the model correction. In the anion complexes $[\text{Fe}(\text{tpps})]^{4-}\text{-O}_2$ and $[\text{Mn}(\text{tpps})]^{4-}\text{-O}_2$, the model correction is positive, indicating that the metal porphyrin anions bind oxygen more strongly than the neutral ones. Such behaviour has been observed in a previous theoretical work,²⁸ and was rationalized by a higher electron density around the metal centre in the metal porphyrin anions.²¹ Indeed, we performed natural population analysis (NPA) calculations⁹⁹ (see Table S5) and found that the atomic charge of the metal centre in $[\text{M}(\text{tpps})]^{4-}$ is slightly more negative than in MP, due to the four external SO₃[–] groups. However, the impact of these groups on the binding enthalpy is minimal (1.7–2.6 kcal mol⁻¹) as they are separated from the porphyrin ring by the phenyl rings. On the other hand, in $[\text{FehemeH}]^+$, the positive charge is located in the substituent $[\text{CH-CH}_3]^+$ attached directly to a β -carbon. This causes a strong reduction of the electron density around Fe, as indicated by NPA charge: 0.879 in FeP versus 1.079 in $[\text{FehemeH}]^+$. Consequently, the binding enthalpy in $[\text{FehemeH}]^+\text{-O}_2$ is reduced by 4.3 kcal mol⁻¹ as compared to the neutral porphyrin. We finally note that experiments⁴⁷ and our calculations both predict a small standard binding enthalpy of O₂ to $[\text{FehemeH}]^+$ (4–5 kcal mol⁻¹).

4 Conclusion

Making use of density functional theory (DFT) and second-order perturbation theory based on density matrix renormalization group (DMRG-CASPT2), we have investigated the electronic structure and standard binding enthalpy of FeP–O₂ and MnP–O₂ with the main focus on the latter system. Different binding modes and electronic states of MnP–O₂ have been studied. We first showed that, as opposed to the end-on configuration of FeP–O₂, MnP–O₂ prefers the side-on configuration. Our theoretical results predict a side-on quartet GS, in agreement with an early prediction of Basolo *et al.* based on IR and EPR^{17,19} and a more recent work of Gallagher *et al.*²⁰ A detailed analysis of the GS wave function revealed a strong charge transfer between MnP and O₂, leading to an assignment of O₂ somewhere

Table 3 Calculated standard binding enthalpies ΔH° (in kcal mol⁻¹) of O₂ to some metal porphyrins

	$\Delta H_{\text{MPO}_2}^\circ$ ^a	ΔE_{MC} ^b	ΔH°	Exp. ^c
[Fe(tpps)] ⁴⁻ -O ₂	8.3	1.7	10.0	9.75±0.33
[FehemeH] ⁺ -O ₂		-4.3	4.0	4.69±0.49
[Mn(tpps)] ⁴⁻ -O ₂	11.9	2.5	14.4	16.10±0.53

^a Standard binding enthalpy $\Delta H_{\text{MPO}_2}^\circ$ of O₂ to MP. ^b Model correction going from MP to the large complexes, calculated with BP86. ^c Experimental standard enthalpy from ref. 21 and ref. 47.

between O₂⁻ and O₂²⁻. Finally, by combining reliable results provided by DMRG-CASPT2 and a model correction obtained from DFT, we estimated the standard binding enthalpies of O₂ to two metal porphyrin anions ([Fe(tpps)]⁴⁻ and [Mn(tpps)]⁴⁻) and one cation [FehemeH]⁺.^{21,47} Our theoretical results are in perfect agreement with the experimental data, with errors less than 2 kcal/mol. Both the experimental and calculated data clearly indicate that O₂ binds more strongly by 4–6 kcal mol⁻¹ to manganese porphyrin than to the corresponding ferrous porphyrin.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This investigation has been supported by grants from the Flemish Science Foundation (FWO). QMP thanks KU Leuven for financial support (Postdoctoral mandates PDM/16/112) and thanks C. Martín-Fernández for fruitful discussions. The computational resources and services used in this work were provided by the VSC (Flemish Supercomputer Center), funded by the Hercules Foundation and the Flemish Government-department EWI. The COST Action ECOSTBio CM1305 from the European Union is also acknowledged.

References

- U. I. Koslowski, I. Abs-Wurmbach, S. Fiechter and P. Bogdanoff, *J. Phys. Chem. C*, 2008, **112**, 15356–15366.
- J. H. Zagal and M. Koper, *Angew. Chem. Int. Edit.*, 2016, **55**, 14510–14521.
- S. Sahu and D. P. Goldberg, *J. Am. Chem. Soc.*, 2016, **138**, 11410–11428.
- J. Masa, K. Ozoemena, W. Schuhmann and J. H. Zagal, *J. Porphyr. Phthalocya.*, 2012, **16**, 761–784.
- D. Den Boer, M. Li, T. Habets, P. Iavicoli, A. E. Rowan, R. J. Nolte, S. Speller, D. B. Amabilino, S. De Feyter and J. A. Elemans, *Nat. Chem.*, 2013, **5**, 621–627.
- H. Chen, M. Ikeda-Saito and S. Shaik, *J. Am. Chem. Soc.*, 2008, **130**, 14778–14790.
- K. P. Jensen, B. O. Roos and U. Ryde, *J. Inorg. Biochem.*, 2005, **99**, 45–54.
- M. Radoń and K. Pierloot, *J. Phys. Chem. A*, 2008, **112**, 11824–11832.
- H. Nakashima, J.-y. Hasegawa and H. Nakatsuji, *J. Comput. Chem.*, 2006, **27**, 1363–1372.
- H. Chen, K.-B. Cho, W. Lai, W. Nam and S. Shaik, *J. Chem. Theory Comput.*, 2012, **8**, 915–926.
- S. Shaik and H. Chen, *J. Biol. Inorg. Chem.*, 2011, **16**, 841–855.
- K. P. Kepp and P. Dasmeh, *J. Phys. Chem. B*, 2013, **117**, 3755–3770.
- M.-S. Liao, M.-J. Huang and J. D. Watts, *Mol. Phys.*, 2011, **109**, 2035–2048.
- C. Rovira, K. Kunc, J. Hutter, P. Ballone and M. Parrinello, *J. Phys. Chem. A*, 1997, **101**, 8914–8925.
- K. Andersson, P.-Å. Malmqvist and B. O. Roos, *J. Chem. Phys.*, 1992, **96**, 1218–1226.
- P. E. Siegbahn, M. R. Blomberg and S.-L. Chen, *J. Chem. Theory Comput.*, 2010, **6**, 2040–2044.
- B. M. Hoffman, T. Szymanski, T. G. Brown and F. Basolo, *J. Am. Chem. Soc.*, 1978, **100**, 7253–7259.
- C. J. Weschler, B. M. Hoffman and F. Basolo, *J. Am. Chem. Soc.*, 1975, **97**, 5278–5280.
- M. W. Urban, K. Nakamoto and F. Basolo, *Inorg. Chem.*, 1982, **21**, 3406–3408.
- A. Gallagher, J. Y. Lee, V. Kathiresan, J. S. Anderson, B. M. Hoffman and D. Harris, *Chem. Sci.*, 2018, **9**, 1596–1603.
- T. Karpuschkin, M. M. Kappes and O. Hampe, *Angew. Chem. Int. Edit.*, 2013, **52**, 10374–10377.
- T. Archipov, J. Kirkland, K. D. Vogiatzis, A. Steiner, G. Niedner-Schatteburg, P. Weis, K. Fink, O. Hampe and M. M. Kappes, *J. Phys. Chem. A*, 2018, ASAP.
- A. Dedieu and M. Rohmer, *J. Am. Chem. Soc.*, 1977, **99**, 8050–8051.
- J. E. Newton and M. B. Hall, *Inorg. Chem.*, 1985, **24**, 2573–2577.
- C. J. Cramer, W. B. Tolman, K. H. Theopold and A. L. Rheingold, *Proc. Natl. Acad. Sci. U.S.A.*, 2003, **100**, 3635–3640.
- M. Tsuda, E. Sy Dy and H. Kasai, *J. Chem. Phys.*, 2005, **122**, 244719.
- M. Tsuda, E. S. Dy and H. Kasai, *Eur. Phys. J. D*, 2006, **38**, 139–141.
- D. Rutkowska-Zbik and M. Witko, *J. Mol. Catal. A: Chem.*, 2006, **258**, 376–380.

- 29 I. Flyagina, K. Hughes, M. Pourkashanian and D. Ingham, *Int. J. Hydrogen Energ.*, 2014, **39**, 21538–21546.
- 30 A. Costa, A. L. P. Silva, R. B. Viana, A. A. Tanaka and J. d. J. G. Varela, *J. Mol. Model.*, 2016, **22**, 217.
- 31 C. A. Reed, J. K. Kouba, C. J. Grimes and S. K. Cheung, *Inorg. Chem.*, 1978, **17**, 2666–2670.
- 32 R. D. Jones, D. A. Summerville and F. Basolo, *J. Am. Chem. Soc.*, 1978, **100**, 4416–4424.
- 33 K. Pierloot, Q. M. Phung and A. Domingo Toro, *J. Chem. Theory Comput.*, 2017, **13**, 537–553.
- 34 Y. Kurashige and T. Yanai, *J. Chem. Phys.*, 2011, **135**, 094104.
- 35 Y. Kurashige, J. Chalupský, T. N. Lan and T. Yanai, *J. Chem. Phys.*, 2014, **141**, 174111.
- 36 S. Wouters, V. Van Speybroeck and D. Van Neck, *J. Chem. Phys.*, 2016, **145**, 054120.
- 37 Q. M. Phung, S. Wouters and K. Pierloot, *J. Chem. Theory Comput.*, 2016, **12**, 4352–4361.
- 38 S. R. White, *Phys. Rev. Lett.*, 1992, **69**, 2863.
- 39 S. R. White, *Phys. Rev. B*, 1993, **48**, 10345.
- 40 S. Wouters and D. Van Neck, *Eur. Phys. J. D*, 2014, **68**, 272.
- 41 T. Yanai, Y. Kurashige, W. Mizukami, J. Chalupský, T. N. Lan and M. Saitow, *Int. J. Quantum Chem.*, 2015, **115**, 283–299.
- 42 R. Olivares-Amaya, W. Hu, N. Nakatani, S. Sharma, J. Yang and G. K.-L. Chan, *J. Chem. Phys.*, 2015, **142**, 034102.
- 43 G. K.-L. Chan and M. Head-Gordon, *J. Chem. Phys.*, 2002, **116**, 4462–4476.
- 44 G. K.-L. Chan and S. Sharma, *Annu. Rev. Phys. Chem.*, 2011, **62**, 465–481.
- 45 U. Schollwöck, *Rev. Mod. Phys.*, 2005, **77**, 259.
- 46 K. H. Marti and M. Reiher, *Z. Phys. Chem.*, 2010, **224**, 583–599.
- 47 N. Shafizadeh, S. Soorkia, G. Gregoire, M. Broquier, M.-E. Crestoni and B. Soep, *Chem. Eur. J.*, 2017, **23**, 13493–13500.
- 48 B. Chiavarino, M. E. Crestoni, S. Fornarini and C. Rovira, *Chem. A Eur. Journal*, 2007, **13**, 776–785.
- 49 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.
- 50 J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822.
- 51 R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Lett.*, 1989, **162**, 165–169.
- 52 M. Dolg, U. Wedig, H. Stoll and H. Preuss, *J. Chem. Phys.*, 1987, **86**, 866–872.
- 53 K. Pierloot, *Mol. Phys.*, 2003, **101**, 2083–2094.
- 54 B. O. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov and P.-O. Widmark, *J. Phys. Chem. A*, 2005, **109**, 6575–6579.
- 55 B. O. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov and P.-O. Widmark, *J. Phys. Chem. A*, 2004, **108**, 2851–2858.
- 56 P.-O. Widmark, P.-Å. Malmqvist and B. O. Roos, *Theor. Chem. Acc.*, 1990, **77**, 291–306.
- 57 N. B. Balabanov and K. A. Peterson, *J. Chem. Phys.*, 2005, **123**, 064107.
- 58 R. A. Kendall, T. H. Dunning Jr and R. J. Harrison, *J. Chem. Phys.*, 1992, **96**, 6796–6806.
- 59 T. H. Dunning Jr, *J. Chem. Phys.*, 1989, **90**, 1007–1023.
- 60 T. Helgaker, W. Klopper, H. Koch and J. Noga, *J. Chem. Phys.*, 1997, **106**, 9639–9646.
- 61 F. Aquilante, P.-Å. Malmqvist, T. B. Pedersen, A. Ghosh and B. O. Roos, *J. Chem. Theory Comput.*, 2008, **4**, 694–702.
- 62 B. A. Hess, *Phys. Rev. A*, 1986, **33**, 3742–3748.
- 63 M. Reiher and A. Wolf, *J. Chem. Phys.*, 2004, **121**, 2037–2047.
- 64 M. Reiher and A. Wolf, *J. Chem. Phys.*, 2004, **121**, 10945–10956.
- 65 S. Wouters, W. Poelmans, P. W. Ayers and D. Van Neck, *Comput. Phys. Commun.*, 2014, **185**, 1501–1514.
- 66 F. Aquilante, J. Autschbach, R. K. Carlson, L. F. Chibotaru, M. G. Delcey, L. De Vico, I. Fdez. Galván, N. Ferré, L. M. Frutos, L. Gagliardi, M. Garavelli, A. Giussani, C. E. Hoyer, G. Li Manni, H. Lischka, D. Ma, P. Å. Malmqvist, T. Müller, A. Nenov, M. Olivucci, T. B. Pedersen, D. Peng, F. Plasser, B. Pritchard, M. Reiher, I. Rivalta, I. Schapiro, J. Segarra-Martí, M. Stenrup, D. G. Truhlar, L. Ungur, A. Valentini, S. Vancoillie, V. Veryazov, V. P. Vysotskiy, O. Weingart, F. Zapata and R. Lindh, *J. Comput. Chem.*, 2016, **37**, 506–541.
- 67 G. Barcza, Ö. Legeza, K. Marti and M. Reiher, *Phys. Rev. A*, 2011, **83**, 012508.
- 68 G. Ghigo, B. O. Roos and P.-Å. Malmqvist, *Chem. Phys. Lett.*, 2004, **396**, 142–149.
- 69 N. Forsberg and P.-Å. Malmqvist, *Chem. Phys. Lett.*, 1997, **274**, 196–204.
- 70 Q. M. Phung, M. Feldt, J. N. Harvey and K. Pierloot, *J. Chem. Theory Comput.*, 2018, ASAP.
- 71 A. A. Holmes, N. M. Tubman and C. Umrigar, *J. Chem. Theory Comput.*, 2016, **12**, 3674–3680.
- 72 S. Sharma, A. A. Holmes, G. Jeanmairet, A. Alavi and C. J. Umrigar, *J. Chem. Theory Comput.*, 2017, **13**, 1595–1604.
- 73 K. Pierloot, H. Zhao and S. Vancoillie, *Inorg. Chem.*, 2010, **49**, 10316–10329.
- 74 L. Mentel and E. Baerends, *J. Chem. Theory Comput.*, 2013, **10**, 252–267.
- 75 P. Piecuch and M. Włoch, *J. Chem. Phys.*, 2005, **123**, 224105.
- 76 M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347–1363.
- 77 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
- 78 S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456–1465.
- 79 N. Strickland and J. N. Harvey, *J. Phys. Chem. B*, 2007, **111**, 841–852.
- 80 J. Ribas-Ariño and J. J. Novoa, *Chem. Commun.*, 2007, 3160–3162.
- 81 S. E. Phillips, *J. Mol. Biol.*, 1980, **142**, 531–554.
- 82 G. Jameson, G. Rodley, W. T. Robinson, R. R. Gagne, C. Reed and J. P. Collman, *Inorg. Chem.*, 1978, **17**, 850–857.
- 83 G. B. Jameson, F. S. Molinaro, J. A. Ibers, J. P. Collman, J. I. Brauman, E. Rose and K. S. Suslick, *J. Am. Chem. Soc.*, 1980,

- 102**, 3224–3237.
- 84 L. Pauling and C. D. Coryell, *Proc. Natl. Acad. Sci. U.S.A.*, 1936, **22**, 210–216.
- 85 J. J. Weiss, *Nature*, 1964, **203**, 183.
- 86 W. A. Goddard and B. D. Olafson, *Proc. Natl. Acad. Sci. U.S.A.*, 1975, **72**, 2335–2339.
- 87 D. S. McClure, *Radiat. Res. Suppl.*, 1960, **2**, 218–242.
- 88 T. Tsai, J. Groves and C. Wu, *J. Chem. Phys.*, 1981, **74**, 4306–4314.
- 89 K. Nakamoto, T. Watanabe, T. Ama and M. Urban, *J. Am. Chem. Soc.*, 1982, **104**, 3744–3745.
- 90 S. Yamamoto and H. Kashiwagi, *Chem. Phys. Lett.*, 1989, **161**, 85–89.
- 91 S. A. Wilson, T. Kroll, R. A. Decreau, R. K. Hocking, M. Lundberg, B. Hedman, K. O. Hodgson and E. I. Solomon, *J. Am. Chem. Soc.*, 2013, **135**, 1124–1136.
- 92 S. A. Wilson, E. Green, I. I. Mathews, M. Benfatto, K. O. Hodgson, B. Hedman and R. Sarangi, *Proc. Natl. Acad. Sci. U.S.A.*, 2013, **110**, 16333–16338.
- 93 R. D. Harcourt, *J. Biol. Inorg. Chem.*, 2014, **19**, 113–123.
- 94 F. A. Lima, T. J. Penfold, R. M. van der Veen, M. Reinhard, R. Abela, I. Tavernelli, U. Rothlisberger, M. Benfatto, C. J. Milne and M. Chergui, *Phys. Chem. Chem. Phys.*, 2014, **16**, 1617–1631.
- 95 K. L. Bren, R. Eisenberg and H. B. Gray, *Proc. Natl. Acad. Sci. U.S.A.*, 2015, **112**, 13123–13127.
- 96 N. Schuth, S. Mebs, D. Huwald, P. Wrzolek, M. Schwalbe, A. Hemschemeier and M. Haumann, *Proc. Natl. Acad. Sci. U.S.A.*, 2017, **114**, 8556–8561.
- 97 J. S. Anderson, A. T. Gallagher, J. A. Mason and T. D. Harris, *J. Am. Chem. Soc.*, 2014, **136**, 16489–16492.
- 98 L. M. Proniewicz, I. R. Paeng and K. Nakamoto, *J. Am. Chem. Soc.*, 1991, **113**, 3294–3303.
- 99 A. E. Reed, R. B. Weinstock and F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 735–746.

$\Delta H_{\text{binding}}$

DMRG-CASPT2

Exp.

(kcal mol⁻¹)

14.4

16.1±0.53

Graphical abstract: The electronic structures of adducts of O₂ and metal porphyrins were thoroughly investigated by highly accurate DMRG-CASPT2.