A Theoretical Study of the Occupied and Unoccupied Electronic Structure of High- and Intermediate-Spin Transition Metal Phthalocyaninato (Pc) Complexes: VPc, CrPc, MnPc, and FePc

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Abstract: The structural, electronic, and spectroscopic properties of high- and intermediate-spin transition metal phthalocyaninato complexes (MPc; M = V, Cr, Mn and Fe) have been theoretically investigated to look into the origin, symmetry and strength of the M–Pc bonding. DFT calculations coupled to the Ziegler’s extended transition state method and to an advanced charge density and bond order analysis allowed us to assess that the M–Pc bonding is dominated by σ interactions, with FePc having the strongest and most covalent M–Pc bond. According to experimental evidence, the lightest MPcs (VPc and CrPc) have a high-spin ground state (GS), while the MnPc and FePc GS spin is intermediate. Insights into the MPc unoccupied electronic structure have been gained by modelling M L2,3-edges X-ray absorption spectroscopy data from the literature through the exploitation of the current Density Functional Theory (DFT) method. Besides the overall agreement between theory and experiment, the DFT/ROCIS results indicate that spectral features lying at the lowest excitation energies (EEs) are systematically generated by electronic states having the same GS spin multiplicity and involving M-based single electronic excitations; just as systematically, the L3-edge higher EE region of all the MPcs herein considered includes electronic states generated by metal-to-ligand-charge-transfer transitions involving the lowest-lying π* orbital (7e_g) of the phthalocyaninato ligand.

Keywords: transition metal phthalocyaninato complexes; X-ray absorption spectroscopy (XAS); Density Functional Theory (DFT); Restricted Open-Shell Configuration Interaction Singles (ROCIS)

1. Introduction

Phthalocyanines (H2Pc) share with porphyrins (H2P), everywhere present “as far as the living world is concerned” [1], the same four nitrogen-based co-ordinative pockets. Even though H2Pc and its metal complexes (MPc) are not present in Nature, they have been attracting great interdisciplinary interest because their technological potential spans over a wide range of applications [2,3]. Besides traditional applications, such as dyestuffs for textiles and inks [3], MPcs are currently used as intrinsic semiconductors, chemical sensors, organic light-emitting diodes, organic photovoltaic cells, thin-film transistors, materials for nonlinear optics, spintronics and laser recording [4–8]. Moreover, bio-inspired oxygen-binding MPcs have been shown as viable substitutes for precious metals in catalysts for the oxygen reduction reaction (ORR) in low-temperature fuel cells [9–12]. As intimate an understanding as possible of the origin, symmetry, and strength of the M–Pc interaction is then mandatory to enhance the efficiency of new MPc-based devices. As such, X-ray absorption spectroscopy (XAS) is unanimously recognized as a valuable tool to probe, element-selectively, the empty electronic structure of M complexes, the M coordinative environment, as well as the nature and the strength of the M–ligand interaction [13–16].
Metal L\(_{2,3}\)-edges’ spectral features are related to the electronic states generated by the electric dipole-allowed 2p \(\rightarrow\) nd excitations [17], thus providing information about the contribution of the M-based nd atomic orbitals (AOs) to the frontier virtual molecular orbitals (VMOs). Metal-based 2p\(^6\) \(\ldots\) nd\(^k\) \(\rightarrow\) 2p\(^5\) \(\ldots\) nd\(^k+1\) excitations create a hole in the M 2p core AOs with an angular momentum quantum number \(\ell = 1\), and spin-orbit coupling (SOC) allows \(\ell\) to couple with \(s\), whose quantum number \(s = 1/2\). Two distinct states are then produced (\(j = 3/2\) and \(j = 1/2\)), with the former (the L\(_3\)-edge) lying at lower excitation energy (EE) and having an intensity approximately twice that of the L\(_2\)-edge associated with \(j = 1/2\). Besides the M L\(_{2,3}\)-edges, the ligand (L) donor atom K-edge XA spectra of ML complexes with partly filled nd AOs are usually characterized by rather intense pre-edge features. These are associated with the electronic states generated by the electric dipole-allowed L-based 1s \(\rightarrow\) mp transitions [17], whose intensity gauges the L mp character of frontier VMOs [18–21]. XAS at the L K-edge thus directly probes the so-called M–L symmetry-restricted covalency [22], affording information complementary to that gatherable by XAS at the M L\(_{2,3}\)-edges. Despite the fact that the L\(_{2,3}\)-edges spectra of ML complexes contain a huge amount of chemical information, their first-principle modelling is theoretically demanding because, besides the ligand field and covalency effects, SOC between the possible many final-state multiplets has to be considered [23–32].

At the very beginning of this century, Koshino et al. [33] recorded the L\(_{2,3}\) excitation spectra of MPc (24 \(\leq Z \leq 29\); \(Z\) corresponds to the atomic number of the metals they considered) by exploiting the inner-shell electron energy-loss spectroscopy (ISEELS); a little over ten years later, Kroll et al. [34] investigated the electronic structure of MPc (25 \(\leq Z \leq 30\)) by combining soft L-edge XAS and 2p photoemission spectroscopy. In addition, few years ago, Eguchi et al. [35] succeeded in the ultra-high vacuum synthesis and XAS characterization of VPc on Ag(111), while neither XAS nor ISEELS data have been so far reported for TiPc to our knowledge.

As a part of a systematic investigation of the electronic properties of energy-targeted materials, some of us have recently investigated their structure/reactivity relationships by exploiting XAS at the N K-edge and at the M L\(_{2,3}\)-edges of diverse MPc (M = V [36,37], Fe [12,38] and Cu [37,39,40]) and CuTPP/CuTPP(F) [41] (H\(_2\)TPP = tetraphenylporphyrin; H\(_2\)TPP(F) = tetrakis(pentafluorophenyl)porphyrin) surface-supported films coupled to quantum mechanical calculations. Two different methodologies were adopted to model the M L\(_{2,3}\)-edges’ features: the current Density Functional Theory variant of the Restricted Open-Shell Configuration Interaction Singles (DFT/ROCIS) method [42] (VPc, FePc and CuPc) and the Relativistic Time-Dependent DFT (RTD-DFT), including SOC with full use of symmetry and correlation effects [43] within the Tamm–Dancoff approximation [44] (CuPc, CuTPP, CuTPP(F)). As such, it has to be noted that, besides L donor atom K-edge XA spectra of ML complexes [39,41,45–47], the RTD-DFT approach may be employed to satisfactorily models the M L\(_{2,3}\)-edges XAS features of closed shell [46,48] and Cu\(^{III}\) complexes. Indeed, the modelling of the Cu\(^{II}\) L\(_{2,3}\)-edges features corresponds, among open shell complexes, to the simplest possible case because the electric dipole allowed 2p\(^6\) \(\ldots\) 3d\(^9\) \(\rightarrow\) 2p\(^5\) \(\ldots\) 3d\(^{10}\) transitions generate a final configuration, which has only two term symbols. The corresponding spectral splitting is dominated by the 2p SOC contribution and the overall energetics and intensities are strongly influenced by ligand-field and covalency, respectively [40]. At variance to that, the RTD-DFT approach is unable to suitably describe SOC in open-shell molecules as explicitly reported in the ADF manual. All the MPcs herein considered (M = V, Cr, Mn and Fe) are open-shell systems with a quite complex electronic structure. A RTD-DFT modelling of their XAS features would then be utterly inadequate, while they can be properly handled by exploiting the module ROCIS of the ORCA program package [42].

In this contribution, a homogeneous modelling of the VPc, CrPc, MnPc, and FePc L\(_{2,3}\)-edges’ features is presented and discussed with the ultimate goal of providing a first-principle rationale of differences characterizing the M–Pc interaction along the investigated series. As such, it can be useful to mention that, with the exception of VPc,
recently synthesized in extreme conditions [35], the remaining MPcs herein considered all have relevant catalytic applications, including the: (i) CO and NO oxidation as well as ORR (CrPc) [49–52]; (ii) oxidation reactions in homogeneous and heterogeneous phase (MnPc) [9]; (iii) N-alkylation [53], C–H amination [54], C–C bond formation [55], synthesis of esters [56] and oximes [57] as well as reduction [58], oxidation [59,60], and radical reactions (FePc) [61]. Moreover, bio-inspired oxygen-binding Fe-macrocycles are particularly appealing as a consequence of their ability to reversibly bind O2, a crucial step in processes such as respiration, photosynthesis or the ORR catalysis [62]. Thus, there is no doubt that a comprehension as intimate as possible of the M–Pc interaction is of paramount importance to design new MPc-like species devoted to specific purposes.

2. Computational Details

The ground state (GS) electronic and structural properties of title molecules have been herein investigated by exploiting the Amsterdam Density Functional (ADF) package [63] within the assumption of an idealized D4h symmetry [17] (see Figure 1), by running spin-unrestricted, nonrelativistic DFT calculations, with generalized gradient corrections self-consistently included through the Becke–Perdew formula [64,65], by adopting a triple-ζ with a polarization function Slater-type basis set for all the atoms, and by freezing the M 1s–2p AO's and the 1s AO of N and C atoms throughout the calculations. MPc optimized Cartesian coordinates are reported in Tables S1–S4 of the Supplementary Materials.

![Schematic representation of a D_{4h} MPc molecule with the atom numbering recommended by the International Union of Pure and Applied Chemistry (IUPAC).](image)

Insights into the origin, symmetry, and strength of the M–Pc interaction have been gained by combining the Nalewajski–Mrozek approach [66–71], well suited to estimating bond multiplicity indices (NM1) in M complexes [66–72], with the Ziegler’s extended transition state (ETS) method [73]. According to the ETS scheme, the MPc bonding energy (BE) may be written as:

\[
BE = - (\Delta E_{es} + \Delta E_{Pauli} + \Delta E_{orb})
\]  

(1)

where \(\Delta E_{es}\) accounts for the pure electrostatic interaction, \(\Delta E_{Pauli}\) represents the destabilizing two-orbital–four-electrons interaction between the occupied orbitals of the interacting fragments (only atomic fragments have been herein considered), and \(\Delta E_{orb}\) corresponds
to the stabilizing interaction between the occupied and empty orbitals of the atomic fragments. In passing, $\Delta E_{\text{orb}}$ may be further decomposed into contributions due to the different irreducible representations (IRs) of the $D_{4h}$ point group, according to

$$\Delta E_{\text{orb}} = \sum_{\chi} \Delta E_{\text{orb}}^{\chi}$$

(2)

The MPc $L_{2,3}$-edges’ XA spectra [33–35] have been modelled by evaluating $EE$s and corresponding oscillator strength distributions ($f(EE)$) for transitions with the M 2p-based MOs as initial spin orbitals (isos), by means of the DFT/ROCIS method [30], which includes SOC in a molecular Russell–Saunders fashion [25], by adopting the B3LYP exchange–correlation (XC) functional [74] for Vpc, CrPc and FePc and the M06 meta-GGA XC [75] for MnPc (vide infra), and by using the def2-TZVP(-f) basis set [76,77]. The combined use of DFT and configuration interaction requires a set of three semi-empirical parameters ($c_1 = 0.18$, $c_2 = 0.20$, and $c_3 = 0.40$), which have been calibrated by Roemelt and Neese [25] for a test set of M $L_{2,3}$-edges. Throughout the M $L_{2,3}$-edges modelling, the resolution of identity approximation has been used with the def-TZVP/J basis set [76,77]. Moreover, the zero-th order regular approximation has been adopted to treat the scalar relativistic effects [78].

Numerical integrations for DFT/ROCIS calculations have been carried out on a dense Lebedev grid (302 points) [79]. In addition, MPc-modelled spectra have been shifted by 10.9 (VPc), 9.8 (CrPc), 8.3 (MnPc) and 13.1 (FePc) eV to superimpose the highest intensity features of the simulated and experimental $L_2,3$-edges. This broadening and the distortion due to the Coster–Kronig Auger decay process [32,80]. This was needed because absolute theoretical $EE$s carry errors arising from DF deficiencies in the core region, one-particle-basis set restrictions and inadequacies in the modelling of spin-free relativistic effects [24].

3. Results and Discussion

3.1. MPc Occupied Electronic Structure

The aim of obtaining an understanding as intimate as possible of the origin, symmetry and strength of the M–Pc interaction may benefit from a preliminary, qualitative description of the MPc frontier orbitals simply based on symmetry arguments and overlap considerations. MPcs are united by the presence of the Pc$^2^-$ ligand whose electronic properties have been thoroughly described elsewhere [81]. Pc$^2^-$ frontier MOs may be split into $\sigma$ and $\pi$ sets. MPc symmetry adapted linear combinations (SALC) of C and N 2p$_e$ (C and N 2p$_v$) are bases for the following $D_{4h}$ IRs: $a_{1g}$, $a_{2g}$, $b_{1g}$, $b_{2g}$, $e_u$ (e$_g$, a$_{1u}$, a$_{2u}$, b$_{1u}$, b$_{2u}$); moreover, among $\pi$ MOs, no a$_{1u}$ SALC of N 2p$_v$ AOs, no b$_{1u}$ SALC of N$^{\text{py}}$ 2p$_v$ AOs and no b$_{2u}$ SALC of N$^m$ 2p$_v$ AOs (see Figure 1) is present. In addition, the four N$^{\text{py}}$ lone pairs pointing towards the centre of the coordinative pocket are bases for the a$_{1g}$, b$_{1g}$ and e$_u$ IRs. In more detail, the two Pc$^2^-$ highest occupied MOs (HOMOs) correspond to the 15b$_{1g}$ MO, $\sigma$ in character and strongly localized on the N$^{\text{py}}$ lone pairs pointing towards the centre of the coordinative pocket, and the 2a$_{1u}$, $\pi$ MO. In this regard, it is noteworthy that the $D_{4h}$ a$_{1u}$ IR is anti-symmetric with respect to the reflections through the $\sigma_v$, $\sigma_d$ and $\sigma_v$ symmetry planes of the $D_{4h}$ point group; the a$_{1u}$, $\pi$ MOs have then a node on symmetry planes passing through N$^{\text{py}}$ and N$^m$ atoms (see Figure 1). As far as the $D_{4h}$ Pc$^2^-$ lowest unoccupied MO (LUMO) is concerned, the 6e$_g$ VMO has a $\pi$ character too.

The presence of the Pc$^2^-$ square planar ligand field lifts the five-fold degeneracy of the M 3d AOs, generating a 3d$_{\epsilon}$ and a 3d$_{\pi}$ set. The former set includes the 21a$_{1g}$ ($z^2$-based) and the 16b$_{1g}$ ($x^2$–$y^2$-based) MOs, while the latter takes in the 14b$_{2g}$ (xy-based) and the 6e$_g$ (xz- and yz-based) ones [17]. Among them, the 21a$_{1g}$ and the 14b$_{2g}$ MOs are substantially M–N$^{\text{py}}$ non-bonding, while the 6e$_g$ and 16b$_{1g}$ MOs are M–N$^{\text{py}}$ $\pi$ and $\sigma$ antibonding, respectively. Relative energy positions of the 3d$_{\epsilon}$/3d$_{\pi}$ spin up ($\uparrow$)/spin down ($\downarrow$) sets in VPC, CrPc, MnPc and FePc are displayed in Figure 2, together with those of selected Pc-based MOs.
The presence of the Pc$^2^-$ square planar ligand field lifts the fivefold degeneracy of the V$^2^+$ ground state (GS) spin multiplicity. Carlotto et al. [36,37] recently proposed a $^4E_g$ high-spin (HS) GS ($a_{1g}^1 b_{2g}^1 e_g^1 b_0^1$; see Figure 2 and Table 1; possible Jahn–Teller distortions [83] associated with orbitally degenerate GS or excited states have not been taken into account), while Eguchi et al. [35] presumed a $^2E_g$ low-spin (LS) GS ($a_{1g}^0 b_{2g}^2 e_g^1 b_0^0$). The $^2E_g$ state generated by the $a_{1g}^0 b_{2g}^2 e_g^1 b_0^0$ configuration is 52.1 (35.5) kcal/mol less stable than the HS $^4E_g$ (LS $^2B_{1g}$) one; moreover, the $^4B_{1g}/^4A_{2g}$ states generated by the constrained $a_{1g}^0 b_{2g}^2 e_g^2 b_0^0$/$a_{1g}^1 b_{2g}^1 e_g^1 b_0^0$/$a_{1g}^1 b_{2g}^2 e_g^2 b_0^0$ configurations are 1.8/1.7 kcal/mol less stable than the $^4E_g$ GS. Consistently with the VPc $a_{1g}^1 b_{2g}^1 e_g^1 b_0^0$ GS configuration, the NMV$_N$Py is quite large (0.64) [36]; as such, since NMV includes both covalent and ionic contributions, it is of some relevance to mention that the V Hirshfeld [84] charge ($Q_V$) amounts to 0.34.

A closer look at the frontier VPc GS electronic structure indicates that all the V 3d-based singly occupied MOs (SOMOs) lie well above the ring-based, V-free, $2a_{1u}$ π doubly occupied MO (DOMO). The ionization energies (IEs) of Vpc frontier MOs are not available in the literature; nevertheless, their values may be estimated by exploiting the Slater

**Figure 2.** Relative energy positions of VPc (a), CrPc (b), MnPc (c) and FePc (d) frontier MOs. Black (↑)/red (↓) arrows refer to Pc-based selected orbitals, while the blue ones correspond to the M 3d-based MOs.

*VPc ground state.* Experimental [35] and theoretical [36,37,82] results disagree about the VPc ground state (GS) spin multiplicity. Carlotto et al. [36,37] recently proposed a $^4E_g$ high-spin (HS) GS ($a_{1g}^1 b_{2g}^1 e_g^1 b_0^1$; see Figure 2 and Table 1; possible Jahn–Teller distortions [83] associated with orbitally degenerate GS or excited states have not been taken into account), while Eguchi et al. [35] presumed a $^2E_g$ low-spin (LS) GS ($a_{1g}^0 b_{2g}^2 e_g^1 b_0^0$). The $^2E_g$ state generated by the $a_{1g}^0 b_{2g}^2 e_g^1 b_0^0$ configuration is 52.1 (35.5) kcal/mol less stable than the HS $^4E_g$ (LS $^2B_{1g}$) one; moreover, the $^4B_{1g}/^4A_{2g}$ states generated by the constrained $a_{1g}^0 b_{2g}^2 e_g^2 b_0^0$/$a_{1g}^1 b_{2g}^1 e_g^1 b_0^0$/$a_{1g}^1 b_{2g}^2 e_g^2 b_0^0$ configurations are 1.8/1.7 kcal/mol less stable than the $^4E_g$ GS. Consistently with the VPc $a_{1g}^1 b_{2g}^1 e_g^1 b_0^0$ GS configuration, the NMV$_N$Py is quite large (0.64) [36]; as such, since NMV includes both covalent and ionic contributions, it is of some relevance to mention that the V Hirshfeld [84] charge ($Q_V$) amounts to 0.34.

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transition state (TS) method [85], which allows the evaluation of excitation/ionization energies “... by means of an artificial state that is halfway between the ground state of an atom or molecule and an excited state” [86]. Interestingly, the lowest VPc TS IE (6.17 eV) is associated with the ionization from the V 3dπ-based 6e g↑ SOMO rather than with the photoemission from the ring-based, V-free, 2a1u π DOMO (6.59 eV). In this regard, it is of value to highlight that in his seminal paper devoted to the investigation of gas-phase photoelectron (PE) spectra of H2Pc and MPc (M = Mg, Fe, Co, Ni, Cu, and Zn), J. Berkowitz pointed out that “... the first ionization potential occurs at ~6.4 eV, and it varies almost imperceptibly from sample to sample, including metal free and MgPc. Therefore, the conclusion seems inescapable that the first ionization potential corresponds to electron ejection from a ring orbital, and not a metal orbital” [87].

Table 1. BP86 ΔBE (kcal/mol) of optimized D4h VPc, CrPc, MnPc and FePc with different spin states. GSs are taken as reference.

| S | VPc | CrPc | MnPc | FePc |
|---|-----|------|------|------|
| 0 | NC  | 31.9 (1A1g) b | 31.9 (1A1g) b |
| 1/2 | 16.6 (2B1g) | 14.9 (2B2u) | 0 (3A2g) g |
| 1 | 25.6 b (3Eg) | 14.9 (2B2u) | 0 (3A2g) g |
| 3/2 | 0 (4Eg) | 0 (4Eg) | NC a |
| 3/2 | 25.6 b (2B1g) | 16.5 (6Eg) |
| 5/2 | NC a | NC a |

a NC stands for non-converged; b Non-Aufbau.

The comparison of the VPc bond lengths and bond angles with those optimized for the other MPc (see Table 2) [88] indicates that the structural perturbations induced by the presence of different MII ions in the Pc2- coordinative pocket are rather minute. CrPc ground state. As already mentioned, CrPc has been attracting great interest as a catalyst for the CO and NO oxidation, as well as for the ORR [49–52], thus making particularly interesting the study of its electronic structure. CrII has a 3d4 configuration, which may generate three spin states with S = 0 (LS), S = 1 (intermediate spin; IS) and S = 2 (HS). Any attempt to optimize the LS state failed (NC, non-converged in Table 1), while the 3Eg IS state, associated with the a1g b1g c2g b0 g↑ 2a1u π configuration, has been found less stable than the 5B1g HS one, generated by the a1g b1g c2g b0 g↑ 2a1u π configuration, by 25.6 kcal/mol (IS and HS CrPc optimized structures are perfectly superimposable). Incidentally, the 3Eg IS state implied a non-Aufbau occupation accompanied by a pseudo reduction (oxidation) of the CrII ion (macrocycle). As such, even though the 5B1g HS GS has been experimentally revealed [89,90] and theoretically predicted [36,82], the localization of VMOs is still controversial. Indeed, SIESTA [91] numerical experiments carried out by Arillo-Flores et al. [82] are consistent with the absence of “... metal contributions to HOMO and LUMO, they principally localize upon the inner ring,” which is certainly correct for the M-free 2a1u π HOMO, but wrong for the 6e g↓ LUMO. In addition, differently from VPc, the ring-based, Cr-free, the 2a1u π DOMO corresponds to the CrPc HOMO (see Figure 2). Analogously to VPc, the IEs of the CrPc frontier MOs are not available in the literature, but, differently from VPc, the lowest TSIE value (6.60 eV) is estimated for the ionization from the ring-based, Cr-free, 2a1u π HOMO.
Upon moving from VPc to CrPc, the GS frontier electronic configuration evolves from $a_1^1 b_2^1 e_1^1 b_0^0$ to $a_1^1 b_1^1 e_1^2 b_0^1$. The addition of an electron to the $3d_{\pi}$-based $6e_g^{\uparrow}\text{MO}$, M–NPy anti-bonding could then be invoked to rationalize the $\text{NMI}_{\text{M–NPy}}$ reduction from 0.64 (see above) to 0.43. Nevertheless, three things need to be kept in mind before drawing conclusions: (i) as already mentioned, NMI includes both covalent and ionic contributions; (ii) $Q_V (0.49)$ is larger than $Q_V (0.34)$; (iii) the $3d_{\pi}$-based $6e_g^{\uparrow}\text{MO}$ is more anti-bonding in CrPc than in VPc (the localization % of the VPc $6e_g^{\uparrow}\text{MO}$ on NPy is negligible; see Figure 3).

Analogously to VPc, no crystallographic data are available in the literature for CrPc; nevertheless, the tiny differences between the CrPc- and VPc-optimized structural parameters seem to indicate that a subtle balance between ionic and anti-bonding covalent contributions to the M–Pc interaction, both of them larger in CrPc than in VPc, takes place.

**MnPc ground state.** Likewise CrPc, LS, IS and HS states are possible; moreover, even though the optimized structural parameters corresponding to different spin states are very similar, the $4^1E_g$ IS state associated to the $a_1^1 b_1^1 e_1^2 b_0^1$ configuration (see Figure 2) has been found more stable than the $6^1E_g$ HS and the $2^1B_{2u}$ LS ones by 16.5 and 14.9 kcal/mol, respectively. As such, it has to be noted that: (i) the MnPc IS GS has been experimentally [94–99] and theoretically [36,100–105] assessed; (ii) the $6^1E_g$ HS state is generated by the $a_1^1 b_1^1 e_1^2 b_0^1 7e_g^1$ configuration; (iii) the $2^1B_{2u}$ LS state has the following occupation numbers: $a_1^1 b_2^1 e_2^1 b_0^1 2a_{1u}^{\uparrow}/a_1^1 b_2^1 e_2^1 b_0^1 2a_{1u}^{\downarrow}$. In this context, it is noteworthy that: (i) both the $7e_g$ and the $2a_{1u}$ MOs are ring-based $\pi$ orbitals, so that the HS (LS) state would imply a pseudo Mn$^\text{II}$ oxidation (reduction) with the Mn 3d-based orbitals occupied by four (six) electrons ($^{1}\text{ISQ}_{\text{Mn}}$, $^{1}\text{LSQ}_{\text{Mn}}$ amount to 0.41, 0.33 and 0.28, respectively); (ii) to our knowledge, only two contributions [33,106] suggested a MnPc HS state. As regards the MnPc IS GS, a further controversy concerns its symmetry, or, equivalently, the occupation

**Table 2.** Theoretical and experimental [88] (in parentheses) structural parameters for $D_{4h}$ VPc, CrPc, MnPc and FePc. Bond lengths/bond angles in Å/$^\circ$, respectively.

|         | M–NPy | NPy–C  | Nm–C  | M–NPy–C | NPy–C–Nm |
|---------|-------|--------|-------|---------|----------|
| VPc $^*$ | 1.996 | 1.392  | 1.333 | 125.4   | 127.4    |
| CrPc $^*$ | 1.982 | 1.387  | 1.330 | 125.6   | 127.5    |
| MnPc $^a$ | 1.952 | 1.396  | 1.324 | 126.1   | 127.4    |
| (1.938)   | (1.392) | (1.315) | (126.2) | (127.6) |
| FePc $^b$ | 1.935 | 1.393  | 1.321 | 126.4   | 127.3    |
| (1.927)   | (1.378) | (1.322) | (126.3) | (127.8) |

* Neither VPc nor CrPc crystallographic data are available in the literature; $^a$ from Ref. [92]; $^b$ from Ref. [93].

![Figure 3. Three-dimensional plots of the VPc and CrPc 6e_g$^{\uparrow}\text{MO}$. Displayed isosurfaces correspond to ± 0.015 e$^{1/2}$Å$^{-3/2}$.](image-url)
numbers of the Mn 3d-based 21a_{1g}, 14b_{2g}, and 6e_{g} MOs. Three different configurations may be considered: \( a_{1g}^1 b_{1g}^1 c_{3g}^1 d_{1g}^0 (4E_g), a_{1g}^1 b_{2g}^2 c_{3g}^0 (4A_{2g}) \) and \( a_{1g}^2 b_{1g}^1 c_{3g}^1 d_{1g}^0 (4B_{1g}) \). In agreement with the theoretical results of Brumboiu et al. [105], the ADF outcomes rule out the \( 4B_{1g} \) state because of its high energy; moreover, it is noteworthy that different experimental studies support either a \( 4E_g \) or a \( 4A_{2g} \) GS. Specifically, XAS evidence [98], magnetic circular dichroism (MCD)/UV-Vis results [95], and XAS/MCD outcomes [99] favour a \( 4E_g \) GS [107], while magnetic susceptibility measurements have been rationalized within the assumption of a \( 4A_{2g} \) GS [95,97], which has been attributed to intermolecular interactions in the MnPc crystal. In agreement with the literature [101], the ADF results herein reported estimate the \( 4E_g \) state to be more stable than the \( 4A_{2g} \) by 7.3 kcal/mol.

Before going on, it is of some relevance to point out that the MnPc \( a_{1g}^1 b_{1g}^1 c_{3g}^1 d_{1g}^0 \) GS configuration implies the presence of a high-lying Mn 3d\( _{\pi} \)-based SOMO\(^{\uparrow} \) well above the ring-based, Mn-free, \( 2a_{1u} \) \( \pi \) DOMO (see Figure 2). As such, no gas-phase photoemission results are available in the literature for MnPc; however, Grobosch et al. [108] were able to record the He(I) photoemission spectrum of an MnPc thin film deposited on polycrystalline Au. Interestingly, they assigned the lowest lying peak of the MnPc valence band photoelectron spectra to MnPc. The x and y axes of the framework they adopted point toward the N atoms toward the N plane. The x and y axes of the framework they adopted point toward the N atoms toward the N plane. In agreement with the literature [101], the ADF results herein reported estimate the \( 4E_g \) state to be more stable than the \( 4A_{2g} \) by 7.3 kcal/mol.

Among the investigated molecules, MnPc is the lightest one for which structural parameters are available [88,92]. The data reported in Table 2 reveal that optimized bond lengths and bond angles fairly reproduce experimental evidence. In this context, the NM\( _{\text{Mn-NPy}} \) value (0.52), just in between the NM\( _{\text{Cr-N}} \) and the NM\( _{\text{I-NPy}} \) values (0.43 and 0.64, respectively), seems to indicate that the M–N\( \pi \) bond-weakening associated with the addition of a further electron to the 3d\( _{\pi} \)-based 6e\( _{g} \) MO is negligible (see Figure S1 of the Supplementary Materials). In addition, it has to be underlined that Q\( _{\text{Mn}} \) (0.33) and Q\( _{\text{V}} \) (0.34) are almost identical.

**FePc ground state.** Similarly to MnPc, experimental [34,110–114] and theoretical [38,104,115] evidence indicates a FePc IS GS whose symmetry is, however, still debated. On the computational side, the IS GS symmetry, inextricably linked to the occupation numbers of frontier MOs, has been found to be extremely sensitive to the adopted XC functional and basis set. Carlotto et al. [38] have proposed a \( ^3E_g \) IS GS, generated by a \( a_{1g}^1 b_{1g}^1 c_{3g}^1 d_{1g}^0 \) configuration, on the basis of numerical experiments carried out by employing the ORCA program package [42], by using the hybrid B3LYP XC–functional [74], by adopting the def2-TZVP(f) basis set [76,77] and the \( c_{1g}, c_{2g}, c_{3g} \) semi-empirical parameters 0.21, 0.49, and 0.29 (hereafter, old set), respectively. In passing, the \( a_{1g}^1 b_{1g}^1 c_{3g}^1 d_{1g}^0 \) GS configuration is a consequence of the orientation of the molecule in the xy plane. The x and y axes of the framework they adopted point toward the N\( ^{m} \) atoms rather than toward the N\( ^{NPy} \) ones (see Figure 1). The four N\( ^{NPy} \) lone pairs were then bases for the \( a_{1g}, b_{2g} \) and \( e_{u} \) IRs rather than for the \( a_{1g}, b_{1g} \) and \( e_{u} \) ones, and the Fe 3d-based VMO accounting for the Fe-N\( ^{NPy} \) anti-bonding interaction corresponded to the 14b\( _{2g} \) level rather than to the 16b\( _{1g} \) one. All the possible configurations compatible with a FePc IS GS have been herein considered. As such, even though the ADF 3B\( _{2g} (a_{1g}^1 b_{1g}^1 c_{3g}^1 d_{1g}^0) \) and the 3E\( _{g} (a_{1g}^1 b_{1g}^1 c_{3g}^1 d_{1g}^0) \) IS states are less stable than the 3A\( _{2g} \) one (\( a_{1g}^2 b_{2g}^1 c_{3g}^1 d_{1g}^0 \)) by minute amounts (1.4 and 1.1 kcal/mol, respectively), it is of some relevance to underline that the \( \Delta E_{\text{orb}} \) (\( \chi = a_{1g}, b_{2g} \) and \( e_{u} \)) of the IS states differ by up to \( \sim230 \) kcal/mol (\( \Delta E_{\text{orb}} = -2584.4, -2810.4 \) and \( -2690.4 \) kcal/mol in the \( 3A_{2g}, 3B_{2g} \) and 3E\( _{g} \) states, respectively). A further ADF 3E\( _{g} \) state may be generated by the \( a_{1g}^2 b_{1g}^1 c_{3g}^1 d_{1g}^0 \) configuration. Besides the non-Aufbau filling of the corresponding electronic levels, the latter 3E\( _{g} \) state is significantly less stable than the 3A\( _{2g} \) GS (12.3 kcal/mol). Additional numerical experiments have been carried out to estimate the FePc BE of the LS and HS states. As far as the former is concerned, it may imply either the \( a_{1g}^1 b_{1g}^2 c_{3g}^1 d_{1g}^0 \) configuration or the \( a_{1g}^2 b_{1g}^1 c_{3g}^1 d_{1g}^0 \). The LS \( a_{1g}^1 b_{1g}^2 c_{3g}^1 d_{1g}^0 \) frozen configuration generates a non-Aufbau energy level filling, and a BE
lower (~32 kcal/mol) than that of the $^{3}_{2}$A$_{2g}$ GS; any attempt to get a converged BE value for the LS $a^2_{g}$ P$_{2g}$ frozen configuration failed. Analogous considerations hold for the HS state.

FePc is the lightest MPc for which gas-phase photoemission spectroscopy data have been recorded [87]. According to experimental evidence, the TSIE of the ring-based, Fe-free, π 2a$_{1u}$ DOMO is the lowest one. Incidentally, its value (6.51 eV) is very close to the one (6.49 eV) estimated by Liao and Scheiner [101], even though a non-relativistic approach has been herein adopted.

According to the experiment in Ref. [93], the shortening of the M–N$_{Py}$ distance upon moving from MnPc to FePc is correctly reproduced (see Table 2). In this context, it is of relevance to mention that $Q_{Fe} = 0.13$; i.e., the smallest value along the investigated series. Such a result, coupled to the NM$_{Fe-N_{Py}}$ = 0.64, ultimately indicates that the Fe–N$_{Py}$ interaction is the most covalent among the molecules we took into account (look at the MPc $\Delta E_{orb}$ values reported in Table 3). In addition, the presence of a strong Fe–N$_{Py}$ covalent $\sigma$ interaction is consistent with the high-energy position of the 16b$_{1g}$ VMO (see Figure 2), which accounts for the $\sigma$ anti-bonding interaction between the Fe 3d$_{x^{2}-y^{2}}$ AO and the b$_{1g}$ SALC of the N$_{Py}$ lone pairs.

Table 3. BP86 $\Delta E_{orb}$ (kcal/mol) of GS D$_{4h}$ MPc herein considered (FePc is taken as a reference).

| V, Cr, Mn, Fe Pcs | a$_{1g}$ | b$_{1g}$ | b$_{2g}$ | e$_{g}$ | $\Delta E_{orb}$ |
|-----------------|-------|-------|-------|-------|-------------|
| VPc             | 100.9 | −86.8 | 81.6  | −16.7 | 79.0        |
| CrPc            | 106.7 | −85.9 | 99.6  | −55.0 | 64.8        |
| MnPc            | 103.8 | −26.8 | 86.2  | −153.9| 9.3         |
| FePc            | 0.0   | 0.0   | 0.0   | 0.0   | 0.0         |

3.2. MPc Unoccupied Electronic Structure

The MPc L$_{2,3}$-edges’ XA spectra [33–35,38] herein modelled have been collected from deposits of different thicknesses, often consisting of randomly oriented and weakly interacting molecules. Thus, according to a procedure successfully tested in the past [36–41,116–120], XAS outcomes have been rationalized by completely neglecting the adsorbate/substrate interactions. Now, before moving to the modelling of the MPc XAS features, a few words about the 2p → 3d excitations simply based on symmetry arguments may be useful to facilitate the forthcoming discussion. In a simplified picture of the 2p → 3d one-electron excitations, the M$^{II}$ electronic configuration moves from the starting $\ldots$ 2p$^{6} \ldots$ 3d$^{k}$ to the ending $\ldots$ 2p$^{5} \ldots$ 3d$^{k+1}$ with 3 ≤ k ≤ 6 for 23 ≤ Z ≤ 26. The electronic states associated to the $\ldots$ 2p$^{5} \ldots$ 3d$^{k+1}$ configurations, straightforwardly obtained by evaluating the $2P \otimes D^{k+1}$ direct products (the whole set of multiplets arising from a particular 3d$^{k+1}$ configuration is herein collectively labelled $D^{k+1}$) [121], are collected in Tables S5–S7 of the Supplementary Materials. The ligand-field, covalent interactions and SOC admixture further split them, to generate totals of 6 × 210 = 1260 (k + 1 = 4), 6 × 252 = 1512 (k + 1 = 5), 6 × 210 = 1260 (k + 1 = 6), and 6 × 120 = 720 (k + 1 = 7) molecular magnetic spin sublevels, respectively. The M$^{II}$ electronic configurations of the MPc herein considered (HS V$^{II}$ 1a$_{1g}$ 1b$_{2g}$ 1c$_{1g}$ 1a$^{0}$, HS Cr$^{II}$ 1a$_{1g}$ 1b$_{2g}$ 1c$_{1g}$ 1a$^{0}$, IS Mn$^{II}$ 1a$_{1g}$ 1b$_{2g}$ 1c$_{1g}$ 1a$^{0}$, IS Fe$^{II}$ 1a$_{1g}$ 1b$_{2g}$ 1c$_{1g}$ 1a$^{0}$) allow us to foresee that the one-electron excitation patterns describing the M$^{II}$ final states in the D$_{4h}$ symmetry should in principle include states having a spin multiplicity either equal to (δS = 0) or lower/higher than (δS = ±1) the GS. The δS = 0 spin-selection rule is slightly relaxed when SOC is considered; more specifically, SOC connects the terms with resultant spins S and S$'$, where |S − S$'$| = 0, 1 [122].

Electric dipole-allowed transitions imply that [17]

$$\Gamma_{GS} \otimes \Gamma_{\mu} \otimes \Gamma_{ES} \supset \Gamma_{Sym},$$

where $\Gamma_{GS}$, $\Gamma_{\mu}$, $\Gamma_{ES}$ and $\Gamma_{Sym}$ correspond to the IRs of the MPc electronic GS, the dipole moment operator (a$_{2u}$ + e$_{u}$) [17], the electronic excited state (\Gamma_{ES} = \Gamma_{iso} \otimes \Gamma_{GS} \otimes \Gamma_{fso}, iso
and $f_{so}$ stand for initial and final spin orbitals, respectively, and the totally symmetric representation of the $D_{4h}$ point group ($a_{1g}$), respectively. Equation (3) may then evolve to

$$\Gamma_{iso} \otimes (a_{2u} + e_u) \otimes \Gamma_{fso} \supset a_{1g},$$

(4)

which implies that, within the adopted approximation, which reduces the complete one-electron excited configuration space (1h–1p space) to the subspace where only the M 2p core electrons (transforming as $a_{2u} + e_u$) [17] are excited, the allowed electric dipole transitions are

$$(a_{2u} \rightarrow a_{1g})^\perp$$

(5)

$$(a_{2u} \rightarrow e_g)^\parallel$$

(6)

$$(e_u \rightarrow e_g)^\perp$$

(7)

$$(e_u \rightarrow a_{1g}/a_{2g}/b_{1g}/b_{2g})^\parallel$$

(8)

where the $\parallel / \perp$ symbols stand for parallel/perpendicular to the molecular $\sigma_h$ plane (see Figure 1).

$\text{VPc L}_3$-edge. To date, only Eguchi et al. have succeeded in synthesizing, even though in extreme conditions, surface-supported mono- and multi-layers of VPc, whose angle-dependent linearly polarized XA spectra at the V L$_{2,3}$-edges are reported in Ref. [35]. As such, a thorough analysis of the $\parallel$ and $\perp$ V L$_{2,3}$-edges components of the VPc and OVPc XA spectra has been recently reported by Carlotto et al. [36,37]. With specific reference to the VPc complex, the authors were able to conclusively assess its spin state by modelling corresponding XAS features for both LS ($S = 1/2$) and HS ($S = 3/2$) states. A brief description of their HS results [36] is herein included to favour the comparison with the modelled spectra of diverse MPcs.

It has been already mentioned that the one-electron excitation pattern describing the $V^\text{II}$ final states in $D_{4h}$ symmetry should be dominated by states which may have (see Table S5 of the Supporting Materials) either a spin multiplicity equal to ($\Delta S = 0$) or lower/higher ($\Delta S = \pm 1$) than the GS one [122]. As such, it has to be underlined that the ORCA B3LYP HS GS corresponds to the $^4A_{2g}$ state generated by the $a_{1g}^1b_{0g}^1e_{2g}^0e_{1g}^0$ electronic configuration. B3LYP/ROCIS outcomes [36,37] indicate that both the $||f(EE)$ and the $\perp f(EE)$ distributions of the L$_3$-edge mainly arise from states having $\Delta S = 0$, while $\Delta S = \pm 1$ contributions are negligible. Moreover, the lowest-lying $||/\perp L_3^1$ features (see Figure 4a) are due to states generated by V 2p $\rightarrow$ SOMOs single electronic excitations. Incidentally, SOMOs correspond to the V 3d-based 6e$_g$ and 21a$_{1g}$ orbitals, while states associated to coupled-single electronic excitations [25,32], mainly involving V 2p $\rightarrow$ SOMOs and SOMOs $\rightarrow$ VMOs excitations, contribute to $||/\perp L_3^1$. SOMOs naturally correspond to the 21a$_{1g}$ and 6e$_g$ MOs, while the VMOs are the V 3d-based 14b$_{2g}$ ($\sim$90%) and the $\pi^*$ Pc-based 7e$_g$ ($\sim$10%) orbitals. In passing, the MPc 7e$_g$ VMO corresponds to the lowest-lying Pc-based $\pi^*$ orbital and metal-to-ligand-charge-transfer (MLCT) transitions (MLCT) transitions in diverse MPc L$_3$-edge spectra (vide infra) involve this VMO. No contribution from V 2p $\rightarrow$ 16b$_{1g}$ excitations is provided to states associated with the VPc L$_3$-edge.

The agreement between the experimental evidence and B3LYP/ROCIS outcomes has been documented in detail elsewhere [36,37]; here, it is sufficient to underline that both the relative positions and relative intensities of spectral features are well reproduced by $||/\perp f(EE)$. Major disagreements between theory and experiment usually affect the L$_2$ region [31]; nonetheless, it deserves mentioning that the B3LYP/ROCIS $||L_2^1\perp L_3^1H^2S\Delta EE$ 6.4 eV, see Figure 4a) fairly reproduces the experimental value (6.9 eV). Any further comment about the VPc L$_2$-edge is herein avoided.
Figure 4. Experimental (dotted lines) and calculated (solid lines) $1^1 - f(EE)$ distributions for $^{1S}VPC$ (a), $^{1S}CrPc$ (b), $^{1S}MnPc$ (c) and $^{1S}FePc$ (d). Blue and red lines correspond to $\parallel$ and $\perp$ components, respectively. Simulated spectra have been shifted by 10.9 ($^{1S}VPC$), 9.8 ($^{1S}CrPc$), 8.3 ($^{1S}MnPc$) and 13.1 ($^{1S}FePc$) eV and have a Gaussian broadening of 1.8 ($^{1S}VPC$), 2.0 ($^{1S}CrPc$), 1.0 ($^{1S}MnPc$) and 1.0 ($^{1S}FePc$) eV. Only the total experimental spectrum (black dotted line) is available for CrPc [33]; MnPc $1^1 - f(EE)$ distributions have been obtained by using the hybrid M06 meta-GGA XC [75] (see text).

CrPc $L_3$-edge. To date, the only CrPc $f(EE)$ distribution for the 2p excitations is the one recorded by Koshino et al. by exploiting ISEELS [33]. Their spectrum includes both the $L_3$- and the $L_2$-edge, but the coarse $EE$ scale they adopted prevents the possibility of revealing the presence of possible structures associated to them; moreover, no information is provided by the authors about the $L_2$–$L_3$ $\Delta EE$. Similarly to VPC, the one-electron excitation pattern describing the Cr final states in the CrPc D$_{4h}$ symmetry is dominated by states which may have (see Table S6 of the Supporting Material) a spin multiplicity either equal to ($\Delta S = 0$) or lower/higher ($\Delta S = \pm 1$) than the GS one. The HS CrPc $1^1 f(EE)$ and $1^1 f(EE)$ B3LYP/ROCIS distributions are superimposed upon the CrPc ISEEL spectrum in Figure 4b. In the $L_3$-edge region, $1^1 - f(EE)$ consists of an intense peak ($L_3^1$) with an evident shoulder on its higher EEs ($L_3^2$, $\Delta EE = 1.40$ eV). Moreover, the B3LYP/ROCIS outcomes also indicate that both $\Delta S = 0$ and $\Delta S = -1$ states, both of them associated with single electronic excitations, contribute...
to the $^{11}/^{1}f(EE)$ distributions. In more detail, $^{11}/^{1}L_3^1$ features are caused by $\Delta S = 0$ states generated by Cr 2p $\rightarrow$ SOMOs transitions, with the whole set of the half-occupied Cr 3d-based orbitals (6e$_g$, 21a$_{1g}$ and 14b$_{2p}$ SOMOs) as $fsos$. At variance with that, the $^{11}/^{1}L_3^2$ shoulders include contributions from both $\Delta S = 0$ (64%) and $\Delta S = -1$ (30%) states. Quintet states have the same origin as those associated with $^{11}/^{1}L_3^1$, while the triplet ones are related to Cr-based 2p $\rightarrow$ 16b$_{1g}$ and MLCT 2p $\rightarrow$ $\pi^*$ Pc-based transitions. As such, it is noteworthy that states associated with the Cr-based 2p $\rightarrow$ 16b$_{1g}$ transition only contribute to $^{1}L_3^2$. Analogously to VPC, any comment about the CrPc $L_2$-edge is herein avoided as it cannot be unambiguously determined by experiment [32]; nevertheless, we underline that the B3LYP/ROCIS $L_2$-$L_3^1$ $^{18}\Delta EE$ (8.6 eV, see Figure 4b) fairly reproduces the experimental value (7.9 eV).

$MnPc$ $L_3$-edge. The MnPc $L_{2,3}$-edges’ XA spectrum recorded by Koshino et al. [33] suffers from the same issues already mentioned for CrPc. Otherwise, the experimental evidence reported by Kroll et al. [34] for MPc (25 $\leq Z \leq$ 30) is much more informative as a consequence of the EE range they showed for each single MPc, thus allowing the detection of the fine structure eventually contributing to spectral features; moreover, both $\perp$ and $\parallel$ polarized XA spectra are reported for each MPc. In the forthcoming discussion, ISEELS outcomes of Koshino et al. will no longer be considered as a reference for the $L_{2,3}$-edges XAS modelling herein presented. At least three well-evident and closely spaced peaks (herein labelled $^{11}/^{1}L_3^1$, $^{11}/^{1}L_3^2$ and $^{11}/^{1}L_3^3$, and lying at $\approx$640.0, $\approx$641.0 and $\approx$643.0 eV, respectively) contribute to the MnPc $^{11}/^{1}$-edge spectrum (see Figure 4c). In addition, the $^{11}/^{1}L_3^3$’ higher EE side is characterized by the presence of an evident shoulder at $\approx$644.0 eV. The $\perp$ light polarization switching is accompanied by a significant relative intensity reduction in spectral features having $EEs$ in between 642 and 644 eV, thus reducing the $^{1}L_3$-edge spectrum to the $^{1}L_3^1$ and $^{1}L_3^2$ peaks with comparable intensity and lying at $\approx$640.5 and $\approx$641.5 eV, respectively (see Figure 4c).

The MnPc B3LYP/ROCIS $^{11}/^{1}f(EE)$ distributions, not herein included, poorly reproduces the $L_3$-edge XA spectrum in terms of number of peaks, relative energy positions and relative intensities. A few years ago, Carlotto et al. [123] tested the efficiencies of several diverse XC functionals (non-hybrid, hybrid and hybrid meta-GGA) in reproducing the $L_{2,3}$-edges’ absorption spectra of Mn complexes. The use of the hybrid M06 meta-GGA XC functional [75] was found to be decisive for a detailed assignment of the Mn(acac)$_2$ 2,3-edges’ absorption spectra of Mn complexes. The satisfactory agreement between the MnPc B3LYP/ROCIS $^{11}/^{1}f(EE)$ distribution (Figure 31), representative of the $^{11}/^{1}L_3^1$ and $^{11}/^{1}L_3^2$ experimental peaks; see Figure 4c) has to be associated to the quartet electronic states ($\Delta S = 0$) generated by single electronic excitations having the whole Mn 2p set as $fsos$ and the low-lying Mn 3d-based 21a$_{1g}$, 14b$_{2g}$ and 6e$_g$ VMOs as $fsos$. At variance with that, electronic states with $\Delta S = 0$ (58%) and $\Delta S = 1$ (24%) contribute to the intense $^{11}/^{1}L_3^3$ feature, while electronic states with $\Delta S = -1$ negligibly contribute to the $^{11}/^{1}L_3^1$ patterns. Former states ($\Delta S = 0$) imply Mn 2p $\rightarrow$ SOMOs (21a$_{1g}$, 14b$_{2g}$ and 6e$_g$) and SOMOs $\rightarrow$ 16b$_{1g}$/7e$_g$ coupled-single excitations [25,32], while the latter ($\Delta S = 1$) are mainly generated by Mn 2p $\rightarrow$ $\pi^*$ Pc-based single electronic excitations. The $\Delta S = 1$ Mn 2p $\rightarrow$ $\pi^*$ Pc-based 4b$_{2u}$ single electronic excitation violates selection rules stated by Eqsns 5–8. As such, it has to be mentioned that i) ORCA calculations have to be run in C$_1$ symmetry and ii) the $f$ value of the $\Delta S = 1$ Mn 2p $\rightarrow$ $\pi^*$ Pc-based 4b$_{2u}$ single electronic excitation is very low.

The satisfactory agreement between $^{11}/^{1}f(EE)$ distributions and experimental evidence [34] prompts us to further detail the proposed assignment. Despite the fact that electronic states generating the $^{11}/^{1}L_3^1$ features of Figure 4c are associated with Mn-based $\Delta S = 0$ 2p $\rightarrow$ 3d single electronic excitations involving the whole 2p set and the low-lying Mn 3d-based $\downarrow$ VMOs, it sounds reasonable that the (1a$_{2u}$ $\rightarrow$ 21a$_{1g}$)$_\perp$ and (1e$_u$ $\rightarrow$ 6e$_g$)$_\perp$
transitions contribute to the L₃ lower EE region more than the (1a₂ → 6eₙ)¹¹, (1eₜ → 21a₁₆)¹¹ and (1eₜ → 14b₂₆)¹¹ ones, while the opposite is true when L₃³ is considered. In fact, once again in agreement with the experimental results of Kroll et al. [34], the electronic states determined by ΔS = 0, 1 coupled-single and single ⊥ polarized electronic transitions provide to the L₃ higher EE region a contribution significantly lower than those || polarized.

DFT/RO CIS calculations fairly reproduce both the L₂–L₃ ΔEE (~10 eV) and the corresponding relative intensities; nevertheless, any detailed assignment of the L₂ feature is herein avoided as it is not unambiguously determined by experimentation [32,80].

FePc L₃-edge. FePc has been the object of a huge number of L₂₃-edges XAS studies [33,34,38,120,124–127]. Among them, Bartolomé et al. [125] investigated the Fe magnetic moment switching in the catalytic ORR of FePc adsorbed on Ag(110) by combining the results of X-ray linear polarized absorption spectroscopy with those of X-ray magnetic circular dichroism at the Fe L₂₃-edges. A detailed analysis of the || and ⊥ Fe L₂₃-edges components of the FePc and FePc(η²-O₂) XA spectra has been recently reported by Carlotto et al. [38] by adopting a computational set-up slightly different from that herein employed. The adopted set of c₁, c₂, and c₃ semi-empirical parameters corresponded to that herein labelled old set; moreover, the saturation of the final-state manifold was obtained by considering forty nonrelativistic roots per multiplicity.

The comparison of the FePc ¹¹/¹σ(f(EE)) distributions (see Figure S2 of the Supplementary Materials) with the literature’s theoretical results [38] proves an evident disagreement. To disentangle the effects induced by the adoption of a particular set of semi-empirical parameters from those generated by the number of nonrelativistic roots per multiplicity, the ¹¹/¹σ(f(EE)) distributions have been again evaluated by using the c₁, c₂, and c₃ old set (see Figure 4d). Besides minor differences, most likely due to the higher number of states and expansion vectors herein adopted in the iterative solution of the CI equations, the ¹¹/¹σ(f(EE)) distributions obtained by adopting c₁ = 0.21, c₂ = 0.49, and c₃ = 0.29 substantially mirror the literature’s ones [38].

According to Carlotto et al. [38], weighty contributions to the ¹¹/¹σ(f(EE)) distributions arise from states having a spin multiplicity either equal to (ΔS = 0) or higher/lower (ΔS = ±1) than the GS one. More specifically, the ¹¹/¹σL₃¹ features lying at the lowest excitation energy (see Figure 4d) are both associated to triplet states (ΔS = 0), and are generated by single electronic excitations with the whole Fe 2p set as isos and the low-lying Fe 3d-based 21a₁₆ VMO and 6eₙ SOMO as f(EE) [38]. Perfectly in agreement with the well-evidenced experimental dichroism [34,38], L₃¹ is much more intense than L₃³, thus indicating that electronic states associated with (a₂u → a₁g)¹/²/(eₜ → eₙ)¹/² excitations contribute much more than the (a₂u → eₙ)¹/²/(eₜ → a₁g)¹/² ones to the lower EE region of the L₃-edge. Excitations with ΔS = 0, −1 comparably participate in states determining L₃² (the theoretical set-up herein adopted makes negligible ΔS = 1 contributions). As such, ΔS = 0 electronic excitations involve the Fe-based 6eₙ VMO and 21a₁₆ VMO, while the ΔS = −1 ones have an MLCT character and imply Pc-based π’ VMOs. Moving to the analysis of the L₃² and L₃³ features, the comparison with the XAS evidence indicates that their excitation energies are slightly overestimated with respect to the L₃¹ ones; moreover, electronic states with ΔS = 0 (71%), 1 (19%) and −1 (7%) contribute to them. In even more detail, both single (44%) and coupled-single (56%) excitations contribute to the prevailing ΔS = 0 states. The former involves Fe-based (2p → 21a₁₆/6eₙ, 2p → 16b₁₆) and MLCT (2p → 7eₙ) transitions, while the latter are Fe-based (2p → SOMOs and SOMOs → 16b₁₆) excitations, determining the states contributing to the L₃² and L₃³ lower excitation energy sides.

The DFT/RO CIS calculations [38] fairly reproduce both the L₂–L₃ ΔEE (~13 eV) and the corresponding relative intensities; nevertheless, any detailed assignment of the L₂ feature is herein avoided as it is not unambiguously determined by experimentation [32,80].
4. Conclusions

The occupied and empty states of HS VPc, CrPc, IS MnPc and FePc have been thoroughly investigated by exploiting the original/homogeneous theoretical results and experimental evidence form the literature. The use of the Hirshfeld charges [84] coupled with the Nalewajski–Mrozek [66–71] approach ultimately indicates that, among the investigated molecules, FePc is characterized by the strongest and most covalent M–Pc σ interaction. Even though Slater’s transition state calculations ultimately confirm the Berkowitz hypothesis that, for FePc, “… the first ionization potential corresponds to electron ejection from a ring orbital, and not a metal orbital”, the extension of the method to lighter MPcs reveals significant differences, the rationale of which lies with the relative energy position of the Pc2−-based and MIII 3d-based occupied/half-occupied MOs. Insights into the MPcs’ virtual electronic structure have been gained by revisiting XAS data from the literature in light of DFT/ROCIS calculations. The higher EE side of the MPc L3-edge XA spectra systematically includes states associated with MLCT transitions, most of them involving the metal 2p → Pc2−-based 7e\(_g\) π* VMO excitations; moreover, the same EE region of all but one of (VPc) the L3-edge XA spectra is characterized by the presence of electronic states associated with M-based 2p → 16b\(_{1g}\) excitations. The agreement between theory and experiment is satisfactory, but it required a “tuning” of the modelling set-up in terms of XC functionals and/or c\(_1\), c\(_2\), and c\(_3\) semiempirical parameters. As a final consideration, we underline that the theoretical outcomes obtained for the HS MPc (VPc and CrPc) are a true challenge for the experimental community called upon to confirm or deny them.

Supplementary Materials: The following are available online at https://www.mdpi.com/2079-4991/11/1/54/s1, Figure S1: 3D plot of the MnPc 6e\(_g\)↓ MO. Displayed isosurfaces correspond to ±0.015 e\(^{1/2}\) × A\(^{-3/2}\); Figure S2: 15FePc 11/1 f(EE) distributions estimated by adopting c\(_1\) = 0.18, c\(_2\) = 0.20, and c\(_3\) = 0.40. Blue and red lines correspond to \(\parallel\) and \(\perp\) components, respectively. Simulated spectra have a Gaussian broadening of 1.5 eV. Table S1: Optimized BP86 Cartesian coordinates for HS VPc; Table S2: Optimized BP86 Cartesian coordinates for HS CrPc; Table S3: Optimized BP86 Cartesian coordinates for IS MnPc; Table S4: Optimized BP86 Cartesian coordinates for IS FePc; Table S5: Symmetries of a 2p\(^5\)3d\(^{4/6}\) system; Table S6: Symmetries of a 2p\(^5\)3d\(^5\) system; Table S7: Symmetries of a 2p\(^5\)3d\(^7\) system.

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