The magnetic behaviour of CoTPP supported on coinage metal surfaces in the presence of small molecules: a molecular cluster study of the surface *trans*-effect.

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**Abstract:** Density Functional Theory combined with the molecular cluster model has been used to investigate the surface *trans*-effect induced by the coordination of small molecules L (L = CO, NH3, NO, NO2 and O2) on the Co local electronic structure of CoTPP surface-supported on coinage metal surfaces (Cu, Ag, and Au). Regardless of whether L has a closed or open shell, its coordination to Co remove the direct interaction between Co and the substrate. The CO and NH3 bonding to CoTPP does not influence the Co local electronic structure, while the NO (NO2 and O2) coordinationinducesa Coreduction(oxidation),generating a 3d8 CoI (3d6 CoIII) magnetically silent closed-shell species.Theoretical outcomes herein reported demonstrate that simple and computationally inexpensive models can be used to not only rationalize but also predict the effects of the Co–L bonding on the magnetic behaviour of CoTPP chemisorbed on coinage metals. The same model can be easily extended to other transition metals or coordinated molecules.

**Keywords:** Density Functional Theory; Transition Metal Porphyrinate Complexes; Molecular Cluster Approximation.

1. Introduction

Among countless adsorbates, transition metal porphyrins and phthalocyanines (hereafter, MP and MPc, respectively) hold a prominent position because of their unique characteristics. Indeed, their conformational flexibility allows them to adopt different structural arrangements on diverse substrates, which may significantly influence their properties. Moreover, the metal centre occupying either the P2- or the Pc2- four-fold coordinative pocket often plays an active role in catalysis and sensors [1-7], while the M *n*d*m* configuration drives the corresponding magnetic behaviour [8-11]. All these features make surface-supported MP and MPc appealing for technological applications including chemical sensors [11-12], storage [13], spintronic/magnetic devices [14-15], and heterogenous catalysis [12,16]. With specific reference to spintronic applications, the ability to finely tune the adsorbate/substrate spin interaction is crucial, demanding a detailed understanding of the interphase electronic properties . In this contest, recent studies [17] have shown that also a chemical stimulus, such as the occupation of a M coordinative vacancy by a small molecule L, may be exploited to control the interphase magnetic properties by “switching on”/”switching off” the spin interactions between L, M and the substrate (S) [18-22]. As such, the competition between the S–M and the M–L interactions has frequently referred to as the surface spin-*trans* effect or more simply as the *trans*-effect [23-24]. Per se, it is noteworthy that, even when dealing with the same MP/MPc surface-supported on the same S, diverse L may generate diverse magnetic behaviours [18-21, 25]. A quantum mechanical modelling of the S–MP–L (S–MPc–L) interphase electronic properties might then be a promising alternative to an inefficient trial-and-error approach for designing new spintronic/magnetic devices [14-15].

In general, numerical experiments carried out by combining the density functional theory (DFT) with the supercell approximation (periodic DFT calculations) provide very accurate results, thus allowing to gain insights into the molecular, electronic andmagnetic properties of the surface-supported MP and MPc [25]. Nevertheless, a major drawback of such an approach concerns its computational cost, which may become prohibitive when several degrees of freedom are considered, or a defective surface is tackled. The magnetic properties of surface-supported MP and MPc are mainly associated with the M oxidation and spin states [26], i.e., with highly localized properties whose modelling within the molecular cluster approximation is not only computationally cheaper than the ordinary periodic model but also physically reasonable [27]. As a matter of fact, the molecular cluster approach allows to look “into the changes in the local bonding situation at the metal centre upon coordination” and “has the advantage that a direct connection to molecular coordination chemistry can be made” [25].

The chemisorption of Co tetraphenyl porphyrin (CoTPP) on diverse metallic S including Ni [23] and coinage metal surfaces (Cu [26,28-29], Ag [20,25,26,30-31], Au [18,20-21,28,30]) has been investigated in detail in the past. In this regard, it has been shown that both Cu and Ag surfaces act as electron donors, thus inducing a CoII  CoI pseudo reduction [20,25,26,28,30,31], while the Au surface does not affect the Co oxidation state [18,20-21,32]. Even though a rationale for these evidences has been provided by periodic DFT numerical experiments [18,21,25,26,29,33], it has been shown that less expensive calculations may adequately model experimental results (“switch on”/”switch off” or *viceversa*) (15,17,25).

Diagram

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**Scheme 1**. A schematic representation of the molecular clusters adopted to model the MS–CoTPP, the CoTPP–L and the MS–CoTPP–L interactions. Grey, white, blue, light blue, red and orange spheres represent C, H, N, Co, O and the MS metal (MS = Cu, Ag or Au) atoms, respectively. A schematic sketch of isolated and interacting systems is reported in the inset.

In this contribution, we present and discuss the outcomes of a series of DFT-based calculations carried out by adopting the molecular cluster model to rationalize and hopefully predict the magnetic behaviour of CoTPP surface-supported on different metallic surfaces (Scheme 1), herein mimicked by a single atom (hereafter, MS; see below), and interacting at the same time with diverse L (CO, NH3, NO, NO2 and O2, Scheme 1).

2. Computational Details

Geometrical parameters of the adopted clusters have been optimized without any constraint by exploiting the Amsterdam Density Functional (ADF) suite of programs [34-35]. Scalar relativistic (SR) spin-unrestricted calculations have been carried out by adopting the Zeroth Order Regular Approximation (ZORA [36-37]), by using the GGA functional BP86 [38-39], by employing a triple-ζ with one polarization function (TZP) Slater-type basis set [40] for all the atoms and by freezing throughout the calculations the C, N and O 1s atomic orbital (AO), the Co and Cu 1s–2p AOs, the Ag 1s–3d AOs and the Au 1s–4d AOs. 3D contour plots (CPs) have been also obtained to get information about the localization and the character of frontier MOs. Finally, bonding energies (*BE*s) have been analysed by means of the Ziegler’s extended transition state [41] method. According to this scheme, *BE*s may be written as

(1)

where, *E*es, *E*Pauli and *E*orb represent contributions due to the pure electrostatic interaction, the Pauli repulsion (hereafter *E*es + *E*Pauli = *E*sr, the steric repulsion), and the orbital interaction, respectively. The last term *E*prep provides information about the energy required to relax the geometrical structure of the fragments CoTPP and L to the geometry they assume in the final cluster. In this regard, it is noteworthy that atomic fragments from which a molecule/cluster is built must be spin-restricted [35]. Both MS–CoTPP and MS–CoTPP–L *BE*s have been then corrected by , which corresponds to the -*BE* between a spin-unrestricted and a spin-restricted atomic fragment. Amendments to *BE*s due to the basis set superposition error have been systematically ignored as their contribution is known to be minor [42].

3. Results and Discussion

The competition between the S–Co and Co–L interactions, as well as its influence on the CoTPP magnetic properties, has been investigated by adopting the following three models: i) MS–CoTPP (MS = Cu, Ag, Au), representing the surface-supported CoTPP; ii) CoTPP–L (L = CO, NH3, NO, NO2, O2), corresponding to the diverse adducts herein considered and iii) MS–CoTPP–L, representing the interphase generated by coordinating L to the surface-supported CoTPP. Optimized Cartesian coordinates of the free L molecules, of the free CoTPP complex, and of the MS–CoTPP, CoTPP–L, and MS–CoTPP–L clusters are reported in Tables S1 – S29 of the Supplementary Materials (SM), while the *BE*s for each molecule/adduct/cluster herein considered are collected in Tables S30 – S37 of the SM.

**3.1 CoTPP on Cu, Ag and Au substrates**. The S–CoTPP interaction has been herein modelled by considering the direct interaction of Co with a single Cu, Ag or Au atom, labelled MS. The adoption of this oversimplified model is inspired by the a-top chemisorption of CoTPP on the (111) surface of coinage metals, a model already adopted by Hieringer et al. [25] to mimic the CoTPP chemisorption on Ag(111). The neutral Cu, Ag and Au atoms have a 3d104s1, 4d105s1 and 5d106s1 electronic configuration, respectively, while the low-spin (LS) CoII species occupying the centre of the TPP2- coordinative pocket carries a single unpaired electron in the Co 3-based molecular orbital (MO) [43]. Thus, the C4v [44] MS-CoTPP cluster may have either 0 or 2 unpaired electrons. In the absence of any constraint on the MS–Co internuclear distance, the antiferromagnetic coupling between the two unpaired electrons is estimated to be significantly and systematically more stable than the ferromagnetic one by 0.71, 0.87 and 0.56 eV for MS = Cu, Ag and Au, respectively. Moreover, when relativistic effects are taken into account [45], the MS–Co internuclear distances and the MS–Co *BE*s corresponding to the spin-paired configuration (see Table S31 of the SM) have the well-known trend within the triad, thus indicating that, among the MS–CoTPP interactions, the Ag–CoTPP one is the weakest and most labile. Incidentally, MS–Co *BEs* amount to 1.17, 0.91 and 1.11 eV for MS = Cu, Ag and Au, respectively.

Although it is of some interest to grasp the main feature of the MS–CoTPP interaction, *BE*s and internuclear distances are unable to rationalize the CoTPP “switch on”  “switch off” magnetism upon chemisorption on Cu [26,28-29,33] and Ag [20,25,26,30-31,33], as well as the absence of any CoTPP demagnetization upon chemisorption on Au [18,20-21,32, 33]. The thorough analysis of the MS-CoTPP frontier molecular orbitals (MOs) turns out to be the Hobson’s choice to get a rationale for the experimental trend. The MS–CoTPP interaction may be roughly described by a two-electrons/two-orbitals model involving the Co 3-based singly-occupied MO (SOMO) and the MS (*n* + 1)s AO (*n* = 4, 5, and 6 for Cu, Ag, and Au, respectively). The analysis of their in-phase and out-of-phase combinations (hereafter, MS–Co and MS–Co\* in Figure 1) suggests that upon chemisorption of CoTPP on Cu and Ag, a CoII + MS0  CoI + MSI pseudo redox reaction takes place (see Figure 1D). Consistently with the presence of a pseudo redox reaction involving a net Cu0  CoII/Ag0  CoII charge transfer, the completely occupied Cu–Co and Ag-Co combinations are mainly localized on the Co 3-based MO, while the empty Cu–Co\* and Ag-Co\* ones are strongly concentrated (> 50%) on the Cu4s-based and Ag5s-based MO, respectively. As such, it can be also useful to mention that the Cu and Ag Hirshfeld charges (Q) [46] of the Cu-CoTPP and Ag-CoTPP C4v clusters amount to 0.19 and 0.24, respectively (see Table S31 of the SM). Incidentally, the LS state foreseen by the molecular cluster model herein adopted and implying the presence of a pseudo 3d8 CoI species well agrees with DFT periodic calculations modelling the CoTPP chemisorption on Cu and Ag surfaces [20,25,26,28-31,33].

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Figure 1: Interaction diagrams between ground state energy levels of CoTPP and the (n + 1)s MS AO for the (A) Cu-CoTPP, (B) Ag-CoTPP and (C) Au-CoTPP C4v clusters. 3D plots of the in-phase and out-of-phase combinations between the Co 3dz2-based MO and the MS (*n* + 1)s AO are also displayed (isosurfaces correspond to ± 0.03 *e*1/2  A-3/2). (D) Sketch of the different charge transfer behaviour along the triad. Colour codes are the same adopted in Scheme 1.

A change of scenery takes place when MS = Au; besides the comparable localization percentage of the Au–Co\* MO on the Co 3 and Au 6s AOs (37% and 42%, respectively), the Au–CoTPP AuQ is close to zero (0.05); in other words, no Au0  CoII charge transfer able to “switch off” the CoTPP magnetization upon chemisorption on Au seems to be present [18,21,32-33]. In summary, the obtained results demonstrate that simple, tiny, and computationally unexpensive models may be exploited to rationalize the magnetic behaviour of CoTPP upon chemisorption on coinage metals.

**3.2 CoTPP–L adducts (L = CO, NH3, NO, NO2, O2)**. The L selection has been ruled by the presence in the literature of experimental and theoretical data pertaining to the CoTPP–L adducts [24-25,33]. The L herein considered may be divided in two groups according to their diamagnetic (CO and NH3, hereafter 0L) or paramagnetic (NO and NO2, 1L; O2, 2L) nature, where the superscripts 0, 1 and 2 simply refer to the number of unpaired electrons carried by L. The valence manifold of the CoTPP–0L adducts is unavoidably characterized by the presence of a single unpaired electron [24,33] carried by Co(II), while the scenery may be more multifaceted when CoTPP–*k*Ladducts (*k* = 1 and 2) are considered.

Both CO and NH3 bind CoTPP vertically, C- and N-down oriented [33]; molecular cluster calculations were then carried out by assuming a C4v and a Cs symmetry [44] for the CoTPP–CO and CoTPP–NH3 species, respectively (see Tables S10 and S11 of the SM). CoTPP–CO and CoTPP–NH3 *BE*s, estimated according to eq. 1 are 0.33 and 0.28 eV, respectively and are reported in Table S32 together with the optimized Co–C/N bond lengths (BLs) and the Nalewajski-Mrozek (NMICo–C/N) bond multiplicity indexes [47-53]. In this regard, it can be useful to mention that the optimized BLC–O passes from 1.139 to 1.157 Å upon moving from the free molecule to the coordinated one, while both the N–H BLs and the H–N–H bond angles (BA) of the coordinated NH3 are negligibly affected upon coordination.

As expected and anticipated, the electronic structure analysis reveals that the 0L coordination to CoTPP does not determine any relevant charge transfer able to modify the CoII oxidation state [24,33]. In addition, the spin population analysis confirms that Co maintains its unpaired electron upon coordination, which remains localized on the Co-based 3d AOs (see Figure 2 and Figure S1 of the SM). Even though only two 0L have been herein considered, it appears likely that the 0L bonding to CoTPP-like and CoPc-like molecules cannot significantly perturb their magnetic properties in general.

Similarly to CoTPP–0L, the 1L coordination to CoTPP has been explored by taking advantage of the available experimental evidence [18]. In more detail, ADF calculations have been run by assuming an N-down orientation for both 1L and by adopting a Cs and a C2v symmetry [44] for the CoTPP–NO and CoTPP–NO2 adducts, respectively (the oxygen atoms of NO and NO2 point toward the meso C atoms of the macrocycle). Optimized geometries (see Tables S12 and S13 of the SM) and *BE*s have been evaluated for both LS (no unpaired electron) and high spin (HS, two unpaired electrons) states.

Starting from CoTPP–NO, its diamagnetic state (the LS state is found to be 1.05 eV more stable than the HS state ) and the peculiar geometry of the [CoNO]8 fragment (the superscript 8 indicates the total number of electrons mostly localized on the Co 3d and the NO \* orbitals) closely resemble the spin state and the crystal structure of the [Co(NO)(Salen)] adduct (Salen = [N,N′-bis(salicylidene)ethylenediamine](https://en.wikipedia.org/wiki/N,N'-bis(salicylidene)ethylenediamine)) [54]. More specifically, the BA is far from being linear both in CoTPP–NO (122.5°, see Table S33 of the SM) and in [Co(NO)(salen)] (127.0° [54]), the Co–N BLs are nearly identical (1.805 Å in CoTPP–NO, see Table S33 of the SM, and 1.807 Å in [Co(NO)(salen)] [54]), and the CoII species lies significantly above the plane passing through the donor atoms of the four-fold coordinative pocket (0.19 Å in CoTPP–NO and 0.25 Å in [Co(NO)(salen)] [54]). Incidentally, the CoTPP–NO highest occupied MO (the 76a' HOMO) is strongly localized on the {CoNO}8 fragment (66%), and it accounts for a bonding interaction,  in character (see Figure S2 of the SM), between the NO\*|| MO and the Co 3d-based AOs lying in the Cs symmetry plane, while the 51a" lowest unoccupied MO (LUMO) is reminiscent of the NO\* MO (see Figure S2 of the SM).

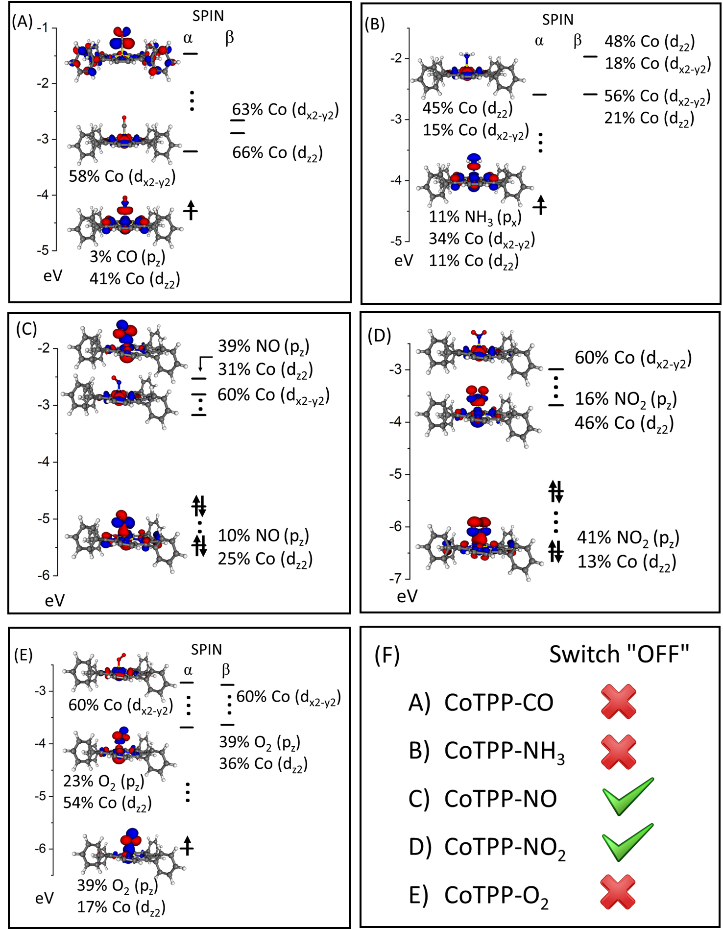


Figure 2. Energy level diagrams of selected MOs for (A) CoTPP-CO, B) CoTPP-NH3, C) CoTPP-NO, D) CoTPP-NO2 and E) CoTPP-O2. Displayed isosurfaces correspond to ± 0.03 *e*1/2  A-3/2. F) Scheme of the “switch off” behaviour upon the L coordination to CoTPP. Vertical dots indicate that some levels, mainly localized on TPP fragment, are omitted. Colour codes are the same adopted in Scheme 1.

Despite all these similarities, the different behaviour of the {CoNO}8 N–O BL upon moving from the free molecule to the coordinated one must be underlined. Theoretical results herein reported show a slight lengthening upon coordination (from 1.166 to 1.185 Å), while the experimental BL of free NO (1.15 Å) perfectly matches the [Co(NO)(salen)] one [54]. It is also worth noting that, even though the geometry of the {CoNO}8 fragment herein optimized fits very well the one obtained by Kim *et al.* for CoTPP–NO by means of periodic DFT calculations [55], their Co–NO *BE* (1.67 eV) is higher than that we obtained by exploiting the molecular cluster model (1.32 eV, see Table S33 of the SM). This difference could be due to the different functional PBE in periodic calculations and the BP86 herein adopted. As a whole, our data indicate that: i) the CoTPP–NO bonding is accompanied by the CoII  CoI “reduction”; ii) the saddle conformation adopted by Kim et al. for the CoTPP–NO on Au(111) takes place independently of the surface presence; iii) if (0.02 eV) and (0.21 eV) are both neglected, the Co–NO *BE* is rather close to the value estimated by Kim *et al.* for the free CoTPP–NO [55].

Notwithstanding the lack of experimental evidence for the CoTPP–NO2 adduct, just under thirty years ago, Rousseau *et al.* [56] tackled the electronic and molecular properties of the EPR silent CoPc–NO2 adduct, pointing out that the Co–NNO2 direct interaction characterized by the Y-shaped coordination of NO2 to CoPc is accompanied by a Co  NO2 charge transfer able to affect the electronic density on the pyrrolic N atom.

Analogously to CoTPP–NO, the CoTPP–NO2 diamagnetic state (LS) is found to be 0.91 eV more stable than the paramagnetic one ; moreover, the optimized geometrical parameters of the C2v [44] CoTPP–NO2 adduct (see Table S33 of the SM) are very close to those adopted by Rousseau *et al.* (Co–NNO2 = 1.91 Å; = 120.0°) [56] for their qualitative extended Hückel numerical experiments. As a result, the NO2 geometry changes upon coordination to CoTPP (the optimized N–O BL lengthens from 1.214 to 1.235 Å and the BA narrows from 133.2° to 125.3°) are perfectly in tune with the above-mentioned Co  NO2 charge transfer. Incidentally, the experimental N–O BL and BA values pass from 1.197 Å and 134.3° in the free NO2 to 1.236 Å and 115.4° in the NO2- nitrite ion [57].

Moving to the electronic properties of CoTPP–NO2, a thorough analysis of its frontier MOs (see Figure 2) reveals that, contrary to the Co–NO bonding, the Co–NO2 one is accompanied by the CoII  CoIII oxidation. In more detail, the CoTPP–NO2 45a1 HOMO is reminiscent of the NO2\*|| SOMO [58] and it is poorly localized (9%) on the Co 3d-based AOs (see Figure 2D), while the 46a1 LUMO is strongly concentrated (46%) on the Co AO. As a whole, even though the coordination to CoTPP of both the 1L herein considered “switches off” the magnetization of the complex (no unpaired electron is present), the 1L quenching mechanism is opposite in NO and NO2: in the former case, it implies the reduction of the CoII centre through the redox reaction NO + COII  NO+ + CoI, while in the latter, the oxidation of the CoII centre through the redox reaction NO2 + COII  NO2- + CoIII takes place.

M complexes with O2 as a ligand have attracted a great interest, mainly driven by the need of looking into the nature and strength of the bonding between dioxygen and M in proteins involved in the O2 carriage in living things. According to their non-linear M–(1-O–O) or bridging M–(-O2) configuration, the two main types of 1:1 M–O2 complexes are usually labelled superoxo and peroxo [57]. The superoxo Co complexes are well structurally characterized [59-65] and Co–(1-O2) and O–O BLs ( BA) ranging between 1.85–1.90 and 1.25–1.35 Å, respectively (115°–125°).

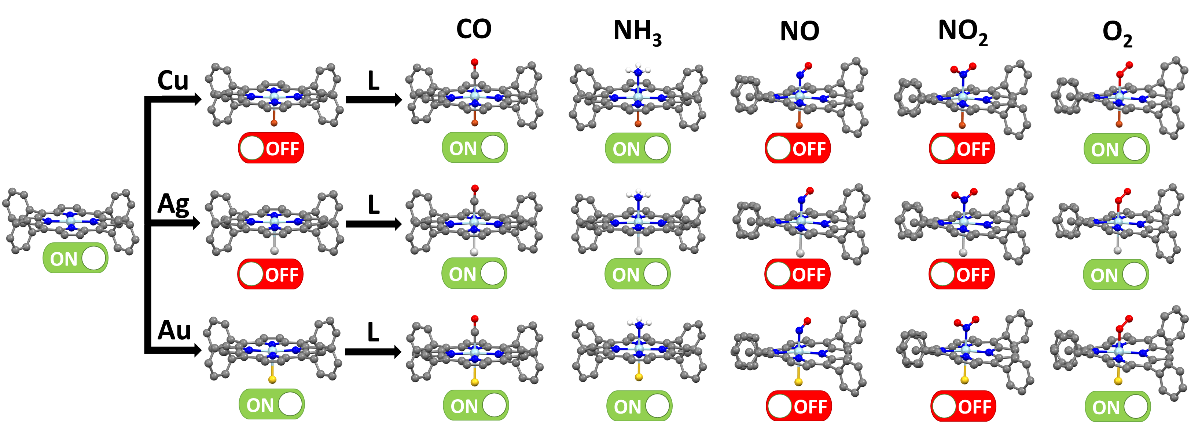
Numerical experiments herein reported have been limited to the superoxo configuration [18] for which both the HS (three unpaired electrons) and LS (one unpaired electron) states have been explored. Analogously to CoTPP–1L, the LS state appears more stable than the HS one (0.49 eV); moreover, the optimized Co–(1-O2) BL and BA (1.858 Å and 119.7°,see Table S34 of the SM) perfectly fall in the above reported ranges (the optimized O–O BLs in the free molecule and in the (1-O2) species are 1.235 and 1.286 Å, respectively). A thorough analysis of the CoTPP–(1-O2) electronic structure reveals that, similarly to CoTPP–NO2, the Co–(1-O2) bonding is accompanied by the CoII  CoIII oxidation with all but one spin orbitals reminiscent of the O2 g MOs [57] (antibonding with respect to the O–O interaction) occupied; the fourth, g-like unoccupied MO (VMO) corresponds to the CoTPP–(1-O2) 51a" LUMO, completely localized (86%) on the spin down () componentof the g spin orbital  to the symmetry plane (see Figure 2E). Consistently with such a picture, the Co spin density is negligible, and the single unpaired electron is completely localized on O2 (see Figure S3 of the SM). Interestingly, even though the number of unpaired electrons does not vary upon moving from CoTPP to CoTPP–(1-O2) and no magnetization “switch off” is then expected (see Figure 2F), the spin configuration of the superoxo adduct is completely different from that of the pristine complex [33].

**3.3 CoTPP–L adducts on Cu, Ag and Au substrates: the *trans*-effect**. Theoretical results pertinent to the MS–CoTPP clusters and the CoTPP–L adducts confirm that simple, tiny, and computationally unexpensive models may be adopted to get information about the magnetic behaviour of CoTPP upon chemisorption on coinage metals as well as on perturbations induced by the coordination of*k*L(*k* = 0, 1, and 2) on the CoTPP frontier orbitals. The feasibility testing of the same approach to explore the effects induced at the same time by chemisorption and coordination on the CoTPP electronic structure is then challenging on one hand and appealing in terms of computational costs on the other hand. As a result, it may be useful to remind that, while both experimental and theoretical data are available in literature, latter studies have been mostly carried out by adopting periodic calculations [18,21,23-25,33,66,67]. The nature, symmetry, and strength of the surface *trans*-effect characterizing the different S–CoTPP–L interphases have been herein investigated by adopting the MS–CoTPP–L clusters, representative of the L interaction with CoTPP deposited on S. MS–CoTPP–L theoretical outcomes have been then compared with literature experimental and/or theoretical data when available.

MS–CoTPP–0Lresults have several common features for both the 0L herein considered, the most relevant being: i) the MS–CoTPP–CO LS state (no unpaired electron) is more stable than the HS one (two unpaired electrons) by 0.58, 0.52, and 0.70 eV for MS = Cu, Ag and Au, respectively; ii) similarly, the MS–CoTPP–NH3 LS state is more stable than the HS one by 0.77, 0.61, and 0.82 eV for MS = Cu, Ag and Au, respectively; iii) both the MS–Co and the Co–C/N *BEs* decrease upon moving from MS–CoTPP and CoTPP–0L to MS–CoTPP–0L (Tables S31, S32, S35, S36 of the SM); iv) both the MS–Co and the Co–C/N BLs increase upon moving from MS–CoTPP and CoTPP–0L to MS–CoTPP–0L for Cu and Ag (Tables S31, S32, S35, S36 of the SM ); v) the MS–Co interaction weakening induced by the 0L coordination is accompanied by the MSI + CoI  MS0 + CoII redox reaction for MS = Cu and Ag; moreover, the MS–CoTPP–0L number of unpaired electrons (disregarding that localized on MS) mirrors the CoTPP–0L one. Incidentally, the doubly occupied MS–CoTPP–CO 30a1 HOMO (MS = Cu and Ag) is strongly localized on the MS (*n* + 1)s/*n* (*n* = 3 and 4 for MS = Cu and Ag, respectively) AOs and the Co 3 AO, while the doubly occupied MS–CoTPP–NH3 74a' HOMO (MS = Cu and Ag) is strongly concentrated on the MS (*n* + 1)s/*n*/*n* (*n* = 3 and 4 for MS = Cu and Ag, respectively) AOs and the Co 3/3 AOs. Incidentally, MS–CoTPP–CO theoretical outcomes perfectly agree with experimental [67] and theoretical [33] literature data.

Even though Au–CoTPP–0L ADF results are also consistent with the presence of CoII (3d7) and Au0 (5d106s1) species, it must be remarked that no Co oxidation state variation takes place upon moving from Au–CoTPP to Au–CoTPP–0L: a consequence of the absence of any CoII  CoI reduction accompanying the chemisorption of CoTPP on Au. As such, it is noteworthy that the lengthening of the Au–Co and Co–C/N BLs upon the L coordination is less significant than that estimated for Cu–CoTPP–0L and Ag–CoTPP–0L (see Tables S31, S32 and S37). Molecular cluster results pertinent to Au–CoTPP–NH3 agree very well with experimental data and periodic calculations [18,21].

As a whole, the magnetization of the MS–CoTPP interphase (MS = Cu and Ag) is “switched on” by the 0L chemisorption, while no variation is expected on passing from Au–CoTPP to Au–CoTPP–0L (see Figure 3, third and fourth columns).

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**Figure 3.** Schematic representation of the magnetic behavior (“switch on”/”switch off”) of the free CoTPP (first column), MS supported CoTPP (MS = Cu, Ag and Au; second column) and of MS supported CoTPP interacting with different L (L = CO, NH3, NO2, NO and O2; third – seventh columns).

Theoretical results obtained for the adducts CoTPP–1L and CoTPP–2L induce us to foresee that the electron exchange taking place at the S–CoTPP–*k*L (*k* = 1 and 2) interphases should not be limited to CoTPP and S but could involve 1L and 2L too. The inspection of Tables S35-S37 of the SM confirms this expectation and clearly shows that the strongest MS–CoTPP–*k*L *trans*-effect is associated to the NO coordination, whose presence: i) decreases the *BE*MS–Co (1.17  0.41 eV, 0.91  0.26 eV, 1.11  0.49 eV, for Cu, Ag and Au, respectively); ii) increases the BLMS–Co (2.27  2.36 Å, 2.47  2.60 Å, 2.46  2.56 Å, for Cu, Ag and Au, respectively). Further insights into the MS–Co and the Co–NO interactions may be gained by referring to the Figure 4, where the MS–CoTPP–*k*L (*k* = 1, 2) simplified energy level diagrams are displayed together with the 3D plots of the MOs mainly localized on the MS-based *n*s AO (*n* = 4, 5 and 6 for Cu, Ag and Au, respectively), the Co-based 3d AOs and the *k*L-based \* fragment MOs.

**Diagram

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**Figure 4.** MS–CoTPP–*K*L (*k* = 1 and 2) schematic energy level diagrams. Displayed isosurfaces of selected MOs 3D plots correspond to ±0.03 *e*1/2  Å-3/2. The energy position of levels mainly localized on the macrocycle is indicated by vertical dots.

The percentages of localization of MO reported in the figure testifies the negligible perturbation induced by the MS presence on the Co–NO bond; moreover, it is noteworthy that the MS (*n*+1)s-based 83a’ SOMO (MS = Cu, *n* = 3; MS = Ag, *n* = 4) has a negligible contribution (≤ 2%) from the Co 3d-based AOs. In addition, both the NO\*⊥-based ↓/↑54a” and the NO\*||-based85a MOs have a VMO character and all but one (the ↓/↑56a” MO) Co 3d-based MOs are completely occupied. The NO *trans*-effect is then characterized by the transfer of the 1L unpaired electron to the MS–CoTPP system, prompting Co and MS to assume a 3d8 (CoI) and *n*d10(*n*+1)s1 (Cu0/Ag0) electronic configuration and taking out any direct MS–Co interaction, in agreement with periodic calculations [33]. Altogether, theoretical outcomes clearly indicate that, even though both the Co oxidation state and electronic configuration are nearly identical in MS–CoTPP, CoTPP–NO and MS–CoTPP–NO, the NO coordination to MS–CoTPP reduces MSI to its elemental oxidation state through the NO  NO+ oxidation contemporary, inhibiting any direct MS–Co bonding (see Tables S35 and S36). The NO coordination does not induce any “switch on” effect on MS–CoTPP because the Co species does not vary its oxidation state and the 1L unpaired electron is used to reduce MS to its elemental oxidation state. It is noteworthy that, both experimental studies and period calculations on S–CoTPP–NO support the molecular cluster outcomes herein reported [66-67].

The comparison of the Au–CoTPP–NO frontier electronic structure with those of the Cu–CoTPP–NO and Ag–CoTPP–NO molecular clusters clearly indicates that the different behavior of Au compared to Cu and Ag has ultimately to be traced back to the diverse MS–CoTPP interaction on passing from Cu/Ag to Au (look at the second column of Figure 3). Au preserves its 5d106s1 electronic configuration along the whole Au  Au–CoTPP  Au–CoTPP–NO path, while the NO  NO+ oxidation (both the NO\*⊥-based and the NO\*||-based Au–CoTPP–NO MOs are empty) provides the electron needed for the CoII CoI reduction. As a whole, the NO coordination to CoTPP chemisorbed on Au is expected to have a “switch off” effect due to the generation of a CoI 3d8 closed shell (see Figure 3).

Although not as strong as that induced by NO coordination, the NO2 *trans*‑effect is quite effective too (see Tables S31, S33, S35-S37 of the SM); in particular, upon moving from MS–CoTPP and CoTPP–NO2 to MS–CoTPP–NO2, the *BE*MS–Co and *BE*Co–N decreasing (see Tables S31, S33 and S35-S37) is accompanied by the BLMS–Co and BLCo–N increasing (see Tables S31, S33 and S35-S37). Common features of the MS–CoTPP–NO2 bonding scheme are: i) the strong localization of the SOMO on the MS (*n*+1)s AO (see Figure 4), which is consistent with a MS *n*d10(*n*+1)s1 elemental electronic configuration (*n* = 3, 4, 5 for MS = Cu, Ag, Au, respectively); ii) the NO2 “closed shell” nature after coordination and then its “nitrite” character (see above); iii) the local “closed shell” electronic configuration (3d6) of Co oxidized by NO2 to CoIII (only the six t2g-like Co-based spin orbitals {the 35b1, 33b2, 46a1 levels in Cu–CoTPP–NO2; the 35b1, 33b2, 48a1 levels in Ag–CoTPP–NO2; the 35b1, 37b2, 50a1 levels in Au–CoTPP–NO2} are occupied). Even though the MS–CoTPP–NO2 magnetic behaviour is closely reminiscent of the CoTPP–NO2 one (no “switch on” effect takes place upon chemisorption of NO2), it must be underlined that, similarly to MS–CoTPP–NO, the Au–CoTPP–NO2 frontier electronic structure differs from the Cu–CoTPP–NO2 and Ag–CoTPP–NO2 ones as a consequence of the diverse MS–CoTPP interaction on passing from Cu/Ag to Au. The NO2 chemisorption on the Au–CoTPP species has then a “switch off” effect on the CoTPP magnetization. Once again these results agree with experimental data and periodic calculations on Au-CoTPP-NO2 [18,21].

Any attempt to optimize the geometry of the MS–CoTPP–(1-O2) cluster with an LS configuration (no unpaired electrons) failed, while the HS (two unpaired electrons) geometry optimization converged rapidly, smoothly, and systematically. Such peculiar behaviour has to be traced back to the electron transfer processes involving at the same time the Co, MS and O2 species (see below).

Aside from the expected decreases in *BE*MS–Co and *BE*Co–O (see Tables S31, S34-S37) and the BLMS–Co and BLCo–C/N/O increasing (see Tables S31, S34-S37) upon moving from MS–CoTPP and CoTPP–(1-O2) to MS–CoTPP–(1-O2), a thorough analysis of the MS–CoTPP–(1-O2) frontier electronic structure revealed: i) the strong localization of the SOMO on the MS (*n*+1)s AO (see Figure 4), which is consistent with a MS *n*d10(*n*+1)s1 elemental electronic configuration (*n* = 3, 4, 5 for MS = Cu, Ag, Au, respectively); ii) the occupied character of all but one (the 54a“ level in Cu–CoTPP–(1-O2); the 54a“ level in Ag–CoTPP–(1-O2); the 57a” level in Au–CoTPP–(1-O2)) g O2-based spin-orbitals (the 50a“, 77a, 81a, 54a“ levels in Cu–CoTPP–(1-O2); the 52a“, 79a, 81a, 54a“ levels in Ag–CoTPP–(1-O2); the 55a”,83a’, 85a’,57a“ in Au–CoTPP–(1-O2)), thus indicating the superoxide nature of the coordinated O2; iii) the occupied character of only six (the 53a“, 54 a“, 77a, 78a, 82a levels in Cu–CoTPP–(1-O2), the 53a“, 54 a“, 79a, 80a, 82a levels in Ag–CoTPP–(1-O2), the 56a”, 57a”83a’, 84a86a levels in Au–CoTPP–(1-O2)) Co 3d-based orbitals, thus awarding a local “closed shell” electronic configuration (3d6) to Co, oxidized to CoIII. through the O2 → O2- reduction.

Despite the O2 coordination to CoTPP adsorbed on coinage metals should be accompanied by a magnetization “switch on” effect, it is noteworthy that unpaired electrons are localized on L rather than on Co (see Figure S3 of the SM).

4. Conclusions

A series of shared features binds the coordination of *k*L to CoTPP surface supported on coinage metal surfaces: i) both *BE*MS–Co and *BE*Co–C/N/O (BLMS–Co and BLCo–C/N/O) decrease (increase) upon moving from MS–CoTPP and CoTPP–L to MS–CoTPP–L; ii) the MS oxidation state in the MS–CoTPP–L cluster is systematically found equal to 0; iii) the local electronic structure of the CoTPP–L fragment in the MS–CoTPP–L cluster is very similar to that of the CoTPP–L adducts; iv) the different MS–CoTPP–L *BE*Co–C/N/O values are scarcely affected by MS thus confirming the leading role played by the *trans*-coordinate ligand in the weakening of the direct MS–Co bonding.

**Supplementary Materials:** .

**Author Contributions:**.

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