



CHEMISTRY JOURNAL OF MOLDOVA.
General, Industrial and Ecological Chemistry

Publication details, including instructions for authors information:
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PORPHYRIN COMPLEXES: A DFT AND NBO
STUDY**

Anan Haj Ichia Arisha ^{a,b,*}

^aDepartment of Organic Chemistry, School of Chemistry, Faculty of
Exact Sciences, Tel Aviv University, Tel Aviv 6997801, Israel

^bDepartment of Education, Beit Berl College, Beit Berl 4490500, Israel

*e-mail: ananarisha@gmail.com

Accepted version posted online: 12 October 2026

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To cite this article: A.H.I. Arisha. Influence of Axial Methoxo and Hydride Ligands on the Structural and Electronic Properties of Cobalt Porphyrin Complexes: A DFT and NBO Study. *Chemistry Journal of Moldova*, 2026, DOI: doi.org/10.19261/cjm.2026.1514

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INFLUENCE OF AXIAL METHOXO AND HYDRIDE LIGANDS ON THE STRUCTURAL AND ELECTRONIC PROPERTIES OF COBALT PORPHYRIN COMPLEXES: A DFT AND NBO STUDY

Anan Haj Ichia Arisha ^{a,b,*}

^aDepartment of Organic Chemistry, School of Chemistry, Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 6997801, Israel

^bDepartment of Education, Beit Berl College, Beit Berl 4490500, Israel

*e-mail: ananarisha@gmail.com

Abstract. Density functional theory and natural bond orbital analysis were used to examine the effects of axial methoxo and hydride ligands on cobalt porphyrin complexes. Neutral and anionic methoxo- and hydride-bound species were compared with the parent cobalt(II) porphyrin. Methoxo coordination produced a charge-sensitive Co–O interaction: reduction lengthened the Co–O bond, weakened ligand-to-metal donor–acceptor interactions, and localized added electron density near the methoxo oxygen atom. In contrast, the Co–H bond underwent only minor structural changes and retained Co 3d_{z²}–H 1s axial σ -bonding character. Reduction of the hydride species mainly caused electronic reorganization and increased spin delocalization over the porphyrin framework. Reduction decreased the calculated frontier-orbital gap from 5.87 to 4.90 eV for the methoxo pair and from 5.90 to 4.28 eV for the hydride pair, with the anionic hydride species showing the smallest gap. The novelty lies in systematically comparing axial-ligand and charge effects in neutral and anionic cobalt porphyrin species.

Keywords: methanol activation, cobalt complexes, spin density, frontier molecular orbitals, donor–acceptor interactions.

Received: 15 July 2026/ Revised final: 22 September 2026/ Accepted: 25 September 2026

Introduction

The development of catalytic transformations based on non-precious metals is an important objective in sustainable synthesis. Cobalt is an attractive alternative to precious metals such as Ru, Rh, Ir, and Pd because of its comparatively low cost, broad availability, and accessible oxidation states, which enable diverse bond-activation and redox processes [1]. Cobalt porphyrins are particularly useful molecular platforms because the rigid porphyrin N4 framework stabilizes the cobalt centre while retaining axial coordination sites for substrates and reaction intermediates. Consequently, their structural and electronic properties can be tuned through changes in oxidation state, overall charge, and axial ligation [2,3].

Methanol is an inexpensive and readily available C1 feedstock, and its catalytic conversion to formaldehyde provides an attractive route for carbon–carbon and carbon–heteroatom bond formation without requiring stoichiometric oxidants. However, methanol activation remains challenging and commonly involves metal–methoxo and metal–hydride intermediates

[4,5]. In the Co(II)-porphyrin-mediated interrupted-borrowing-hydrogen reaction reported by Biswal *et al.*, mechanistic experiments led to the proposal that a protonated cobalt–porphyrin methoxide intermediate generates formaldehyde together with a cobalt hydride species [5]. The resulting hydride was proposed to react with methanol, thereby releasing H₂ and regenerating the active catalytic system. Thus, methoxo- and hydride-bound cobalt porphyrin species are likely to play central roles in methanol activation.

Axial ligation is a key factor controlling cobalt porphyrin reactivity. The identity of the axial ligand can influence the metal–ligand bond strength, coordination geometry, electron density at cobalt, redox properties, spin-state distribution, and metal–ligand covalency [3,6]. Nevertheless, the distinct structural and electronic effects of axial methoxo and hydride ligands, particularly in neutral and anionic cobalt porphyrin species, remain insufficiently understood in the context of methanol activation.

Recent experimental, review, and computational studies have highlighted the structural diversity and electronic tunability of

cobalt porphyrin systems, including substituted, axially ligated, and related porphyrin derivatives [7-10]. Further theoretical investigations have demonstrated that axial ligation, peripheral substitution, metal identity, and spin state can substantially influence the geometric and electronic properties of metalloporphyrin systems [11-15]. In this work, density functional theory and Natural Bond Orbital analyses were used to compare the parent Co(II) porphyrin complex with neutral and anionic methoxo- and hydride-bound cobalt porphyrin complexes. The aim was to determine how axial-ligand identity and overall charge affect the molecular geometry, cobalt-centred orbital structure, metal-ligand bonding, charge and spin distributions, and frontier-orbital properties. These results provide an electronic-structure basis for understanding the possible roles of methoxo and hydride intermediates in cobalt-porphyrin-mediated methanol activation. The unsubstituted porphine framework was deliberately selected as a minimal reference model to isolate the intrinsic effects of axial-ligand identity and overall charge on the cobalt centre without additional electronic or steric contributions from peripheral substituents. This simplified model therefore provides a well-defined baseline for evaluating methoxo- and hydride-induced changes in cobalt porphyrin electronic structure. However, the quantitative trends obtained for the unsubstituted porphine framework should not be assumed to be directly transferable to meso-substituted or β -substituted porphyrins. Peripheral substitution can modify the electronic and steric environment of the cobalt centre, including its redox properties and frontier-orbital energies [9,11,15]. Accordingly, the present calculations should be regarded as a reference framework for evaluating substituent effects in more complex cobalt porphyrin derivatives. The present conclusions are also specific to cobalt and should not be directly generalized to porphyrin complexes of other metals. Changing the metal centre alters the d-electron configuration, accessible oxidation and spin states, metal-ligand covalency, and axial-ligand affinity. Consequently, systems based on Zn, Mg, Fe, Cr, or heavier metals may exhibit substantially different structural and electronic responses to methoxo or hydride coordination. Extension of the present trends to other metalloporphyrins therefore requires separate metal-specific calculations. The distinctive contribution of the present study is the systematic side-by-side comparison of neutral and anionic methoxo- and hydride-bound cobalt porphine species within a common computational

framework, allowing the effects of axial-ligand identity and overall charge to be evaluated separately.

Computational methods

All density functional theory (DFT) calculations were performed using Gaussian 16, Revision C.01, and GaussView 6.1.1 [16,17]. The ω B97X-D functional and the def2-TZVPP basis set were used for all calculations. All calculations were carried out in the gas phase. The ω B97X-D functional was selected because its long-range corrected hybrid formulation and empirical dispersion treatment are well suited for describing both metal-ligand interactions and noncovalent contributions in transition-metal porphyrin systems. The def2-TZVPP basis set was employed to provide a balanced triple- ζ description with polarization functions for both the cobalt centre and the ligand framework. Gas-phase calculations were used to isolate the intrinsic structural and electronic effects of axial-ligand identity and overall charge without introducing solvent-specific stabilization effects. Accordingly, the calculated trends should be interpreted primarily as intrinsic gas-phase properties of the model complexes.

The five species considered in this work were selected as computational model systems rather than as newly synthesized compounds. Complex **1** is the parent cobalt porphine, $C_{20}H_{12}CoN_4$ (neutral, doublet). Complexes **2** and **3** are the neutral and anionic methoxo-bound species, $C_{21}H_{15}CoN_4O$ and $[C_{21}H_{15}CoN_4O]^-$, in singlet and doublet states, respectively. Complexes **4** and **5** are the corresponding neutral and anionic hydride-bound species, $C_{20}H_{13}CoN_4$ and $[C_{20}H_{13}CoN_4]^-$, in singlet and doublet states, respectively. These five species were selected to provide a controlled comparison of the effects of axial-ligand identity and overall charge on the structural and electronic properties of the cobalt porphyrin framework.

The parent cobalt(II) porphyrin complex **1** and the anionic cobalt hydride complex **5** were optimized and subjected to harmonic vibrational-frequency analysis in single Opt+Freq calculations. For complexes **2–4**, geometry optimizations and vibrational-frequency calculations were performed as separate calculations. This procedure was adopted because combined optimization and frequency calculations showed convergence difficulties for the porphyrin-containing systems.

For complexes **2** and **3**, additional optimization settings were required to obtain fully converged minima, including calculation of the force constants at the first point, tight optimization

criteria, a maximum of 200 optimization cycles, and an ultrafine numerical integration grid [Opt=(CalcFC,Tight,MaxCycles=200), Int=UltraFine]. These settings were employed because complexes **2** and **3** exhibited greater convergence sensitivity during geometry optimization than the other complexes, and the additional force-constant evaluation, tighter convergence criteria, and extended optimization cycle limit improved the robustness of the optimization procedure.

All final optimized structures were confirmed as minima by the absence of imaginary vibrational frequencies. Natural Bond Orbital (NBO) analyses were performed at the same level of theory using the Pop=(NBO,SaveNBOs) keyword. The Cartesian coordinates of all optimized complexes are provided in Tables S6–S10, and the thermodynamic parameters are summarized in Table S11 in the Supplementary Material.

Results and discussion

Axial ligand coordination can significantly influence the electron density, spin state, metal-ligand covalency, and redox properties of cobalt porphyrin complexes. Therefore, comparing methoxy- and hydride-bound species provides insight into how axial ligand identity and overall charge control the electronic structure of the cobalt centre.

The optimized geometry and electronic features of cobalt(II) porphyrin (complex **1**) were first characterized to investigate its structural and electronic properties. The initial step involved a full geometry optimization, yielding the structure of complex **1** in the doublet spin state ($S = \frac{1}{2}$). Figure 1 presents the optimized geometry, and selected bond lengths and angles are summarized in Table 1.

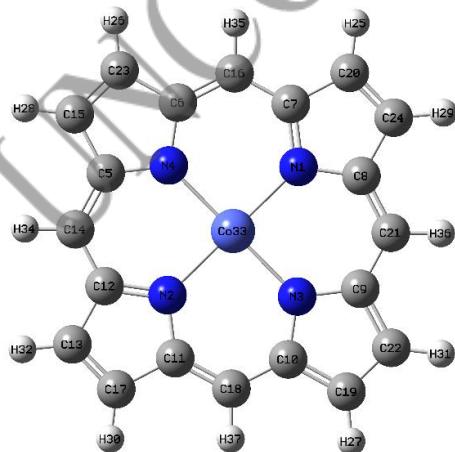


Figure 1. Optimized structure of complex **1**.

Table 1

Some selected geometric parameters of complex **1.**

<i>Bond lengths (Å)</i>			
Co33–N1	1.971	N1–C7	1.367
C7–C20	1.433	C20–C24	1.348
C7–C16	1.374	C20–H25	1.078
<i>Bond angles (°)</i>			
Co33–N1–C7	127.44	N1–C7–C16	125.49
N1–C7–C20	110.76	C7–C20–C24	106.68
C7–C16–C6	124.14	C7–C20–H25	124.49
C7–C16–H35	117.93	C16–C7–C20	123.75
N1–Co33–N2	180.00	N1–Co33–N4	90.00

The calculated Co–N bond length of complex **1** (1.971 Å) is in close agreement with the value reported for low-spin Co-porphine (1.96 Å) [18]. This agreement supports the reliability of the optimized geometry. The electronic structure of complex **1** was then examined using Natural Bond Orbital (NBO) analysis to gain deeper insight into the orbital interactions that define its electronic properties.

NBO analysis provides a quantitative framework to describe donor→acceptor electron-delocalization (hyperconjugation), intramolecular H-bonding, intramolecular charge transfer, and bond–antibond interactions. The stabilization associated with each interaction is estimated by second-order perturbation theory from the Fock matrix in the NBO basis, according to Eq.(1).

$$E(2) = \Delta E_{i,j} = -q_i \frac{F^2(i,j)}{\varepsilon_i - \varepsilon_j} \quad (1)$$

where, q_i is the occupancy of the donor NBO;
 $F(i,j)$ is the off-diagonal Fock element;
 $\varepsilon_i, \varepsilon_j$ are the diagonal (orbital) energies.

Larger $E(2)$ values indicate stronger donor→acceptor coupling and greater delocalization.

Table 2 summarizes the five cobalt-centred d-type orbitals of the Co(II) porphyrin complex, assigned according to their spatial characteristics obtained from the NBO analysis. The dx^2-y^2 orbital is singly occupied and exhibits the lowest energy among the identified d-type orbitals. This orbital lies in the porphyrin plane and is oriented between the Co–N bonding axes, resulting in limited overlap with the porphyrin nitrogen orbitals. In contrast, the remaining d-type orbitals are fully occupied, with approximately two electrons each.

The complete second-order perturbation analysis of the Fock matrix in the NBO basis for complex **1** (α spin) is provided in Table S1 in the Supplementary Material. The porphyrinic nitrogen

sp^2 lone pairs are the principal donors to cobalt-centred acceptor orbitals. The strongest interactions involve donation into the cobalt d_{xy} and $4s$ acceptor orbitals, whereas the interactions with the Co $4p_y$ and $4p_x$ orbitals are weaker and essentially equivalent. No significant Co→porphyrin donor–acceptor interactions were identified. Representative orbital depictions are shown in Figures S1 and S2 in the Supplementary Material.

These NBO results consistently identify the $d_{x^2-y^2}$ orbital as the singly occupied cobalt-centred orbital, with no significant Co→porphyrin donor–acceptor interactions identified in the NBO second-order perturbation analysis and limited spatial overlap with the porphyrin framework. This electronic description is further supported by the spin-density analysis.

Figure 2 displays the spin-density distribution of complex **1**. The analysis indicates that the unpaired electron is mainly localized on the cobalt centre and is associated predominantly with

the $d_{x^2-y^2}$ orbital, with minor spin-density contributions extending along the z-axis and toward the porphyrin framework.

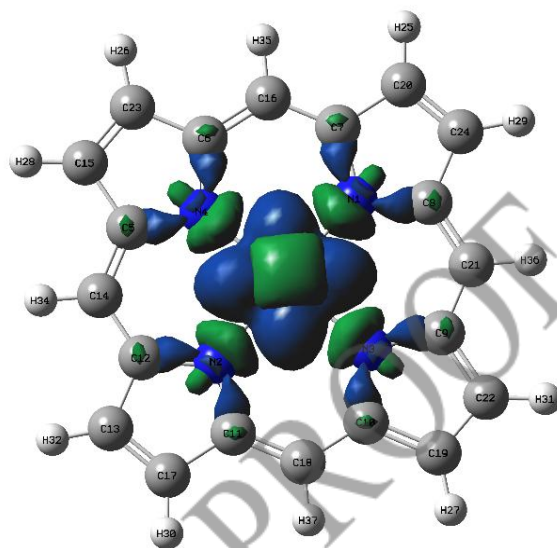


Figure 2. Spin density distribution of complex **1**.

Table 2

Cobalt-centred d-type orbitals of Co(II) porphyrin from NBO analysis: energies and occupancies.

Orbital Type	α Energy (eV)	β Energy (eV)	Occupancy	Orbital Diagram
$d_{x^2-y^2}$	−11.82	—	1.00	
d_{yz}	−9.14	−8.31	2.00	
d_{xz}	−9.14	−8.31	2.00	
d_{z^2}	−8.36	−7.52	2.00	
d_{xy}	−4.94	−4.05	2.00	

Overall, the combined structural, orbital, and spin-density analyses highlight the central role of the cobalt $d_{x^2-y^2}$ orbital in defining the electronic structure of complex **1**. The strong localization of the unpaired electron at the cobalt centre, together with only minor delocalization toward the porphyrin framework, establishes complex **1** as a suitable reference for evaluating the electronic effects of axial methoxo and hydride coordination.

Building on the results obtained for complex **1**, the structural and electronic effects of methoxo coordination on the cobalt porphyrin framework were then investigated. Accordingly, two species were considered: neutral methoxo complex **2**, optimized in the singlet spin state, and the corresponding anionic complex **3**, optimized in the doublet spin state. Figure 3 presents the optimized structures of complexes **2** and **3**. The selected

geometric parameters of complexes **2** and **3** are listed in Table 3.

A noticeable geometric difference between complexes **2** and **3** is observed mainly at the cobalt–methoxo binding site. Complex **2** exhibits a significantly shorter Co–O bond than complex **3** (1.808 Å vs. 2.041 Å), indicating stronger metal–ligand interaction in the neutral species. The Co–N bond distances in complex **3** are also slightly longer, whereas the internal geometric parameters of the porphyrin framework remain nearly unchanged. These results suggest that the main structural effect of the overall charge is localized at the cobalt coordination site rather than in the porphyrin skeleton.

The cobalt-centred d-type orbitals of complex **2** are summarized in Table 4. The mixed $d_{x^2-y^2}/d_{xy}$ orbital is dominated by $d_{x^2-y^2}$ character, with a smaller d_{xy} contribution.

Table 3

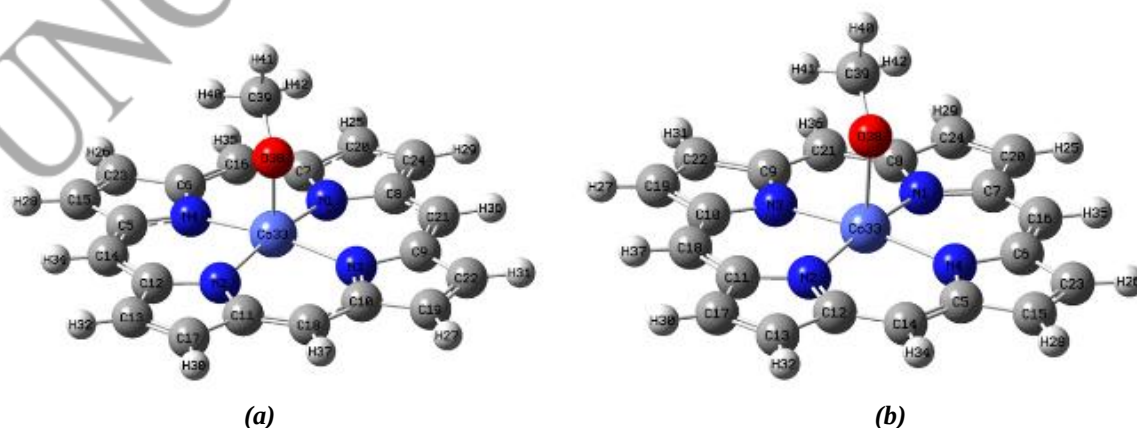
Some selected geometric parameters of **2** and **3**.

Bond lengths (Å)					
	Complex 2	Complex 3		Complex 2	Complex 3
Co33–N1	1.976	2.001	N1–C7	1.367	1.358
C7–C20	1.432	1.440	C20–C24	1.349	1.350
C7–C16	1.374	1.380	C20–H25	1.078	1.079
Co33–O38	1.808	2.041	O38–C39	1.388	1.357
Bond angles (°)					
	Complex 2	Complex 3		Complex 2	Complex 3
Co33–N1–C7	127.36	126.75	N1–C7–C16	125.50	125.45
N1–C7–C20	110.77	110.59	C7–C20–C24	106.65	106.50
C7–C16–C6	124.18	124.99	C7–C20–H25	124.55	124.79
C7–C16–H35	117.89	117.48	C16–C7–C20	123.71	123.96
N1–Co33–N2	169.51	171.38	N1–Co33–N4	89.67	89.78
N1–Co33–O38	99.48	96.25	Co33–O38–C39	118.94	119.41

Table 4

Cobalt-centred d-type orbitals of complex **2** from NBO analysis: energies and occupancies.

Orbital Type	Energy (eV)	Occupancy
$d_{x^2-y^2}$ (68.5%) + d_{xy} (31.4%)	-10.50	2
d_{yz}	-10.46	2
d_{xz}	-10.48	2

Figure 3. Optimized structures of complexes **2** (a) and complexes **3** (b).

The Co–O bond arises from the overlap between a cobalt hybrid orbital, composed of 4s (18.53%), 4p (29.43%), and 3d (52.03%) character, with the 3d contribution being predominantly $3d_{z^2}$, and an oxygen hybrid orbital composed mainly of $2p_z$ (88.08%) with a smaller 2s contribution (11.79%). The overall contributions to the Co–O bonding NBO are 25.47% from cobalt and 74.53% from oxygen. Figure S3 shows the Co–O bonding orbital, which has an energy of -14.09 eV and an occupancy of 1.84779 electrons.

The NBO analysis identifies three occupied cobalt-centred d-type orbitals in complex **2**. Among these orbitals, one is a mixed d-type NBO dominated by $d_{x^2-y^2}$ character, with a smaller contribution from d_{xy} . The predominant participation of the Co ($3d_{z^2}$) orbital in the axial Co–O bonding NBO indicates that the Co–O bond involves a cobalt hybrid orbital whose 3d contribution is mainly d_{z^2} in character and is oriented along the Co–O axis toward the methoxo ligand.

To further elucidate the donor–acceptor interactions that stabilize complex **2**, a second-order perturbation analysis of the Fock matrix in the NBO basis was performed, and the most significant interactions are summarized in Table S2. The second-order perturbation analysis shows that the porphyrinic nitrogen lone pairs are the principal donors to cobalt-centred acceptor orbitals in complex **2**. The strongest interaction involves donation from the N sp^2 lone pair into a cobalt acceptor orbital with predominant d_{xy} character. Substantial donation is also observed into the Co 4s acceptor orbital, whereas donation into the Co 4p acceptor orbitals is weaker but still significant. These interactions demonstrate the important role of the porphyrinic nitrogen atoms in stabilizing the cobalt center through equatorial ligand-to-metal donation. In addition, the σ (O38–C39) $\rightarrow$ LP* (Co) ($4p_z$) interaction indicates electronic coupling between the coordinated methoxo ligand and the cobalt centre along the axial Co–O direction.

To evaluate the effect of reduction and the resulting negative charge on the electronic structure of the methoxo-bound cobalt porphyrin,

the NBO analysis was extended to the corresponding anionic complex **3**. The cobalt-centred d-type orbitals of complex **3** are summarized in Table 5. Table 5 shows that the cobalt-centred d-type NBOs of complex **3** differ between the α - and β -spin manifolds. In the α -spin manifold, the two lowest-energy orbitals contain mixed d_{z^2} and $d_{x^2-y^2}$ character, whereas the β -spin manifold contains a predominantly $d_{x^2-y^2}$ orbital. In contrast to complex **2**, appreciable d_{z^2} character is retained in the cobalt-centred d-type NBOs of complex **3**, indicating redistribution of the cobalt electron density upon reduction.

The donor–acceptor interactions obtained from the second-order perturbation analysis for complex **3** (α -spin) are summarized in Table S3. The donor–acceptor interactions in complex **3** retain the same qualitative ligand-to-metal donation pattern observed for complex **2** but are generally weaker. In particular, reduction weakens both the equatorial donation from the porphyrinic nitrogen lone pairs to cobalt-centred acceptor orbitals and the axial electronic coupling between the methoxo ligand and the cobalt center, consistent with the weaker Co–O interaction in the anionic complex.

The spin-density distribution of complex **3** is shown in Figure 4. Figure 4 shows that the spin density in complex **3** is primarily localized at the cobalt centre, with additional delocalization over the porphyrin framework and toward the axial methoxo ligand.

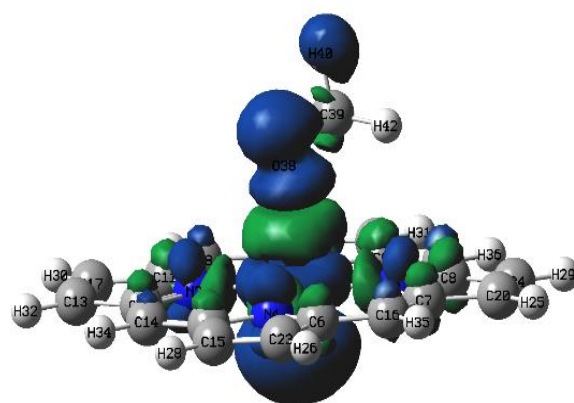


Figure 4. Spin-density distribution of complex **3**.

Table 5

Cobalt-centered d-type NBOs of complex **3** from NBO analysis: energies and occupancies.

Orbital Type	α Energy (eV)	Occupancy	Orbital Type	β Energy (eV)	Occupancy
d_{z^2} (62%)+ $d_{x^2-y^2}$ (37%)	-5.66	1			
d_{z^2} (36.4%)+ $d_{x^2-y^2}$ (62.8%)	-5.69	1	$d_{x^2-y^2}$	-5.03	1
d_{yz}	-4.95	1	d_{yz}	-4.30	1
d_{xz}	-4.94	1	d_{xz}	-4.31	1
d_{xy}	1.24	0.30	d_{xy}	2.27	0.27
			d_{z^2}	4.63	0.20

The optimized structures of the neutral cobalt hydride complex **4**, optimized in the singlet spin state, and the corresponding anionic complex **5**, optimized in the doublet spin state, are presented in Figure 5, while selected geometric parameters are summarized in Table 6. The geometric parameters of complexes **4** and **5** are very similar. In particular, the Co–H bond length changes only slightly upon reduction (1.409 Å in complex **4** and 1.413 Å in complex **5**), while the Co–N distances and the porphyrin framework show only minor variations. Thus, in contrast to the methoxo complexes, the overall charge has little effect on the hydride coordination geometry.

The cobalt-centred d-type orbitals of complex **4** are summarized in Table 7. Table 7 identifies three fully occupied cobalt-centred d-type NBOs with d_{xy} , d_{yz} , and d_{xz} character. In

contrast, the $d_{x^2-y^2}$ NBO is only partially occupied, indicating a lower electron population in this in-plane cobalt orbital relative to the other d-type NBOs.

The Co–H bonding NBO has an occupancy of 2 electrons and an energy of –11.27 eV. It is composed of 65.06% cobalt and 34.94% hydride character; the cobalt contribution arises mainly from the $3d_{z^2}$ orbital (85.35%), with smaller contributions from $4p_z$ (7.62%) and $4s$ (7.03%), whereas the hydride contribution is almost entirely derived from its $1s$ orbital (99.26%). The Co–H bonding orbital of complex **4** is shown in Figure S4.

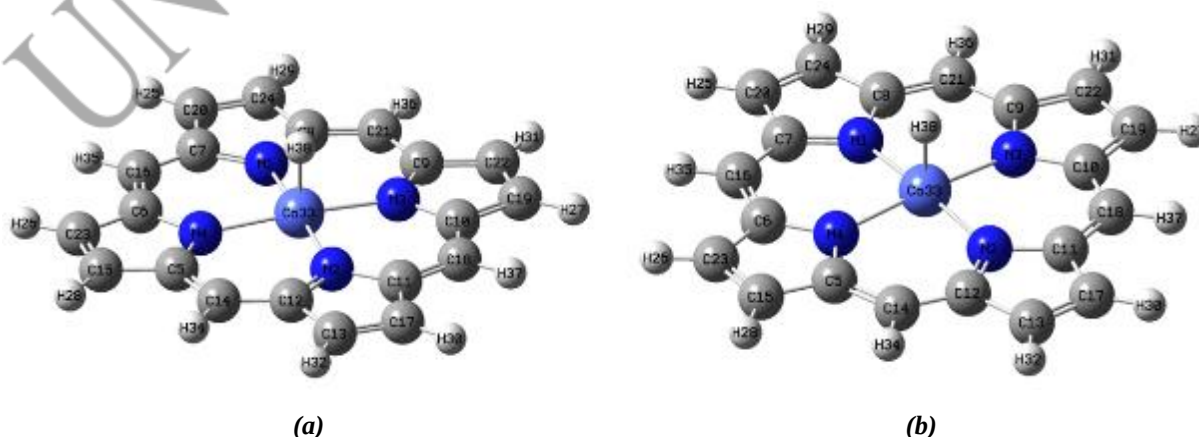
The predominance of Co ($3d_{z^2}$) and H ($1s$) character in the Co–H bonding NBO is consistent with an axial sigma-bonding interaction along the Co–H direction.

Table 6

Selected geometric parameters of complexes 4 and 5 .					
<i>Bond lengths (Å)</i>					
	Complex 4	Complex 5		Complex 4	Complex 5
Co33–N1	1.971	1.978	N1–C7	1.366	1.375
C7–C20	1.434	1.446	C20–C24	1.348	1.342
C7–C16	1.374	1.359	C20–H25	1.078	1.079
Co33–H38	1.409	1.413			
<i>Bond angles (°)</i>					
	Complex 4	Complex 5		Complex 4	Complex 5
Co33–N1–C7	127.46	127.19	N1–C7–C16	125.42	126.19
N1–C7–C20	110.90	110.26	C7–C20–C24	106.61	107.01
C7–C16–C6	124.15	124.35	C7–C20–H25	124.56	124.19
C7–C16–H35	117.92	118.07	C16–C7–C20	123.68	123.55
N1–Co33–N2	175.51	174.62	N1–Co33–N4	89.91	89.89
N1–Co33–H38	92.25	92.69			

Table 7

Cobalt-centred d-type orbitals of complex 4 from NBO analysis: energies and occupancies.		
<i>Orbital Type</i>	<i>Energy (eV)</i>	<i>Occupancy</i>
d_{xy}	–9.74	2
d_{yz}	–9.53	2
d_{xz}	–9.53	2
$d_{x^2-y^2}$	–3.46	0.71

Figure 5. Optimized structures of complexes **4** (a) and complexes **5** (b).

The donor–acceptor interactions obtained from the second-order perturbation analysis for complex **4** are summarized in Table S4. The second-order perturbation analysis reveals strong equatorial donation from the porphyrinic nitrogen lone pairs to cobalt-centred acceptor orbitals. In addition, the $\sigma^*(\text{Co-H}) \rightarrow \text{LP}^*(\text{Co}) (4s)$ pronounced interaction indicates substantial electronic coupling involving the Co–H antibonding orbital and the cobalt (4s) acceptor orbital.

The cobalt-centred d-type orbitals of complex **5** are summarized in Table 8. Table 8 shows that the low-energy cobalt-centred d-type orbitals of complex **5** are the d_{xy} , d_{xz} , d_{yz} orbitals. These orbitals are occupied in both the α - and β -spin manifolds and display nearly identical α/β energies, indicating that they remain effectively spin-paired upon reduction. In contrast to neutral hydride complex **4**, where the corresponding occupied d-type orbitals occur at substantially lower energies (approximately –9.5 eV), these orbitals in complex **5** are shifted upward to approximately –6.0 eV. This pronounced energy increase reflects the electronic effect of the additional negative charge on the cobalt centre. The $d_{x^2-y^2}$ type orbital in complex **5** remains only weakly occupied. Its limited population indicates that reduction mainly raises the energies of the cobalt-centred d-type orbitals without substantially altering their overall occupation pattern.

In the α -spin manifold, the Co–H bonding NBO has an occupancy of 1.00 electron and an energy of –6.79 eV. The bond is polarized toward cobalt, which contributes 59.51%, whereas the hydride contributes 40.49%. The cobalt hybrid is composed of 15.98% 4s, 15.04% 4p, and 68.97% 3d character, with the 3d contribution dominated by the $3d_{z^2}$ orbital and a minor admixture of $3d_{x^2-y^2}$ character. The hydride contribution is almost entirely derived from the H 1s orbital (99.30%). The Co–H bonding NBO in the β -spin manifold has an occupancy of 1.00 electron and an energy of –7.73 eV. Its electronic composition is similar to that observed for the α -spin counterpart, with predominant Co $3d_{z^2}$ and H 1s character. The Co–H bonding NBO in complex **5** retains the

axial σ -bonding character observed for complex **4** and is dominated by Co $3d_{z^2}$ and H 1s contributions. Reduction decreases the polarization of the bond toward cobalt and raises the energies of the Co–H bonding NBOs. Because the Co–H bond length changes only slightly, these results indicate that the effect of the additional negative charge on the Co–H unit is primarily electronic rather than structural.

The second-order perturbation analysis of the Fock matrix in the NBO basis for complex **5** (β -spin) is summarized in Table S5. The second-order perturbation analysis of complex **5** retains the same general ligand-to-metal donation pattern observed for neutral hydride complex **4**. However, the interactions involving porphyrinic nitrogen lone pairs and cobalt-centred acceptor orbitals are markedly weaker in the anionic complex, indicating reduced equatorial stabilization of the cobalt centre upon reduction. The $\sigma^*(\text{Co-H}) \rightarrow \text{LP}^*(\text{Co})(4s)$ interaction remains the strongest interaction but is substantially decreased relative to complex **4**, indicating reduced donor–acceptor coupling involving the Co–H antibonding orbital. In addition, the $\text{LP}^*(\text{Co}) (4p_y) \rightarrow \sigma^*(\text{Co-H})$ interaction indicates electronic coupling between the cobalt $4p_y$ and Co–H antibonding orbitals. Overall, the added negative charge weakens both the equatorial ligand-to-metal donation and the antibonding orbital interactions associated with the Co–H bond.

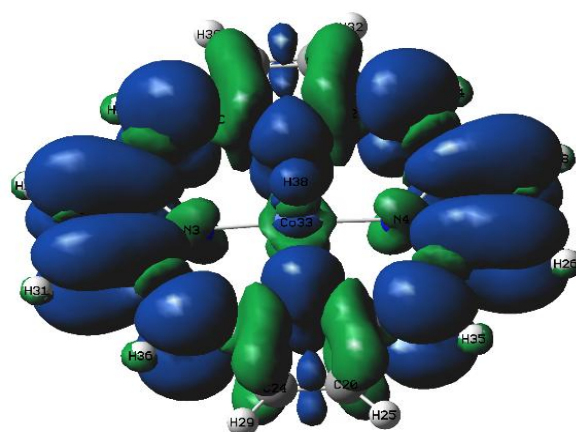


Figure 6. Spin-density distribution of complex **5**.

Table 8

Cobalt-centred d-type orbitals of complex **5** from NBO analysis: energies and occupancies.

Orbital Type	α Energy (eV)	Occupancy	Orbital Type	β Energy (eV)	Occupancy
d_{xz}	-6.08	1	d_{xz}	-5.88	1
d_{xy}	-6.14	1	d_{xy}	-6.14	1
d_{yz}	-5.98	1	d_{yz}	-5.97	1
$s(43.16\%)+p(11.51\%)+d_{z^2}$ $(6.21\%)+d_{x^2-y^2}(38.86\%)+$	9.73	0.22	$d_{x^2-y^2}$	0.17	0.35

The spin-density distribution of complex **5** is presented in Figure 6. Figure 6 shows that the spin density in complex **5** is predominantly delocalized over the porphyrin framework, with a smaller contribution around the cobalt–hydride unit. This distribution indicates that the unpaired electron introduced upon reduction is not localized exclusively at cobalt, which is consistent with the weak occupation of the cobalt $d_{x^2-y^2}$ type orbital observed in Table 8.

The molecular electrostatic potential (ESP) maps of complexes **3** and **5**, mapped onto the electron-density isosurfaces, are presented in Figure 7. Figure 7 reveals distinct electrostatic-potential distributions for the two anionic complexes. In complex **3**, the most negative potential is localized primarily around the axial methoxo ligand, particularly near the oxygen atom, consistent with its substantial negative charge. In contrast, complex **5** displays a more diffuse electrostatic-potential distribution over the hydride-containing porphyrin framework. The narrower potential range observed for complex **5** further indicates a less pronounced charge separation than in complex **3**. These results show that the identity of the axial ligand strongly controls the localization of negative charge in the anionic cobalt porphyrin complexes. For completeness, the molecular electrostatic potential

(ESP) maps of the neutral methoxo and hydride complexes **2** and **4** are provided in Figure S5 in the Supplementary Material.

The Natural Population Analysis (NPA) charges of complexes **1–5** are summarized in Table 9, showing that axial ligand coordination strongly modifies the charge distribution at the cobalt centre. Methoxo coordination in complex **2** markedly decreases the positive NPA charge on cobalt relative to complex **1**, consistent with strong electron donation from the axial methoxo ligand. Upon reduction to complex **3**, the cobalt charge becomes substantially more positive, whereas the methoxo oxygen atom and the representative porphyrinic nitrogen atom N1 become more negative, indicating that the added electron density is mainly delocalized over the ligand environment rather than localized at cobalt.

In contrast, the Co and hydride charges change only slightly between hydride complexes **4** and **5**. This result is consistent with the nearly unchanged Co–H bond length and indicates that reduction has a limited effect on the charge distribution within the Co–H unit. Overall, the NPA results support the ESP analysis and show that the axial methoxo ligand promotes stronger localization of negative charge than the hydride ligand.

Table 9

Natural population analysis (NPA) charges of complexes **1–5**.

Complex	Co33	N1	O38	C39	H40	H41	H38
1	0.759	−0.476					
2	0.143	−0.157	−0.409	−0.098	0.069	0.099	
3	0.703	−0.433	−0.826	−0.191	0.108	0.095	
4	0.311	−0.423					0.208
5	0.334	−0.469					0.178

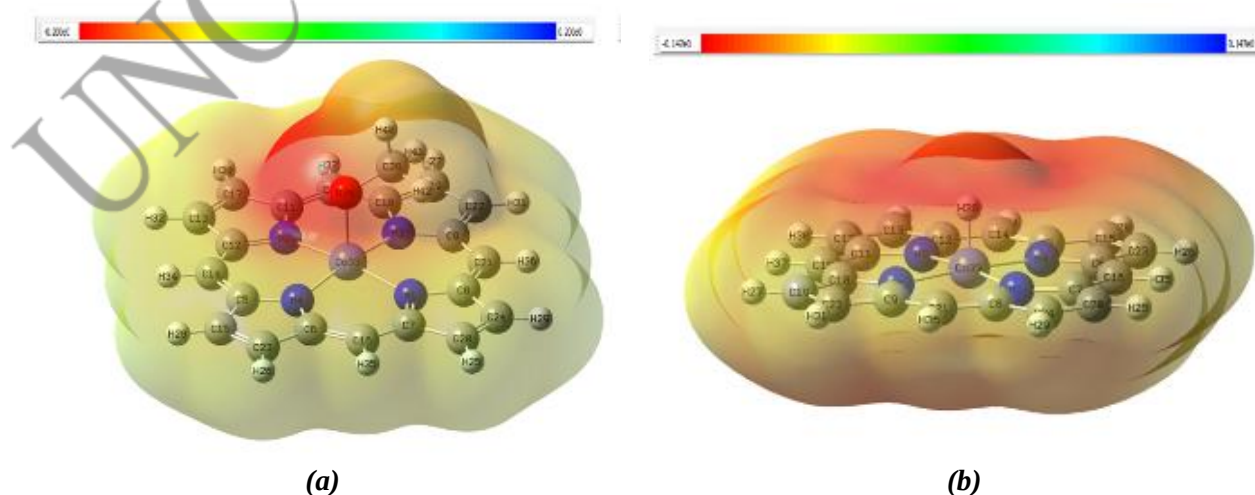


Figure 7. Molecular electrostatic potential (ESP) maps of complexes **3** (a) and complexes **5** (b) mapped onto the electron density isosurfaces.

Table 10

Calculated Kohn–Sham frontier orbital energies and energy gaps of complexes 1–5.

Complex	HOMO/SOMO energy (eV)	LUMO energy (eV)	Frontier orbital energy gap, ΔE (eV)
1	SOMO (α): -6.91	LUMO (α): -1.02	5.89
2	HOMO = -6.94	LUMO = -1.07	5.87
3	SOMO (α) = -2.65	LUMO (α) = 2.25	4.90
4	HOMO = -6.88	LUMO = -0.98	5.90
5	SOMO (α) = -1.52	LUMO (α) = 2.76	4.28

To compare the frontier electronic structures of complexes 1–5, the energies of the HOMO or SOMO, the LUMO, and the corresponding frontier-orbital energy gaps were evaluated and are summarized in Table 10. Table 10 shows that the neutral complexes 1, 2, and 4 have nearly identical calculated Kohn–Sham frontier-orbital energy gaps, indicating that axial methoxo or hydride coordination has only a limited effect on the frontier electronic structure in the neutral state. In contrast, reduction substantially decreases the calculated frontier-orbital energy gap in the anionic complexes 3 and 5. Complex 5 has the smallest gap, indicating that, within the calculated Kohn–Sham orbital-energy description, hydride coordination combined with negative charge produces the closest frontier orbitals among the complexes studied.

Conclusions

This DFT and NBO study demonstrates that both axial-ligand identity and overall charge strongly influence the structural and electronic properties of cobalt porphyrin complexes. The parent Co(II) porphyrin complex 1 exhibits a cobalt-centred unpaired electron that is predominantly associated with the $d_{x^2-y^2}$ orbital, providing a suitable electronic reference for evaluating the effects of axial coordination.

Methoxo coordination produces a pronounced response to reduction. The neutral methoxo complex 2 displays a short Co–O bond and strong axial and equatorial ligand-to-metal interactions. Upon reduction to complex 3, the Co–O bond is substantially elongated, the donor–acceptor interactions involving both the porphyrin nitrogen atoms and the methoxo ligand are weakened, and the additional electron density is mainly distributed over the ligand environment, particularly around the methoxo oxygen atom. Thus, the methoxo ligand strongly controls both the structural and electrostatic response of the cobalt porphyrin framework to reduction.

In contrast, the hydride complexes 4 and 5 show only minor structural changes upon reduction. The Co–H bond retains its axial

sigma-bonding character, dominated by overlap between Co ($3d_{z^2}$) and H (1s) orbitals. Reduction primarily affects the electronic structure of the Co–H unit, raising the energies of the cobalt-centred orbitals and weakening the associated donor–acceptor interactions, while leaving the Co–H bond length nearly unchanged. The spin density in anionic complex 5 is mainly delocalized over the porphyrin framework rather than being localized exclusively at cobalt.

The frontier-orbital analysis further shows that the neutral complexes have nearly identical calculated HOMO/SOMO–LUMO gaps, whereas reduction decreases these gaps substantially. Complex 5 has the smallest calculated frontier-orbital gap among the species examined. Overall, the results establish that axial methoxo and hydride ligands induce distinct electronic responses in cobalt porphyrins: methoxo coordination produces a strongly charge-sensitive Co–O interaction, whereas hydride coordination preserves the Co–H geometry but undergoes substantial electronic reorganization upon reduction. These findings provide an electronic-structure basis for future mechanistic studies of cobalt porphyrin systems involved in methanol activation and related transformations.

Supplementary information

Supplementary data are available free of charge at <http://cjm.ichem.md> as PDF file.

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