

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

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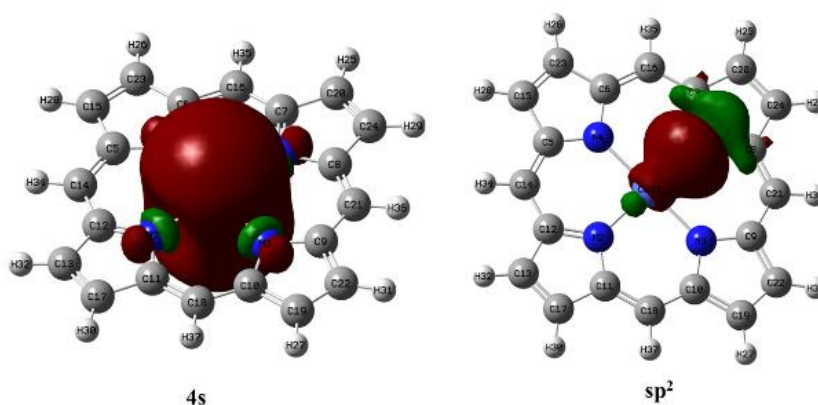


Figure S1. Co 4s orbital and porphyrin N sp² lone-pair orbital in complex 1.

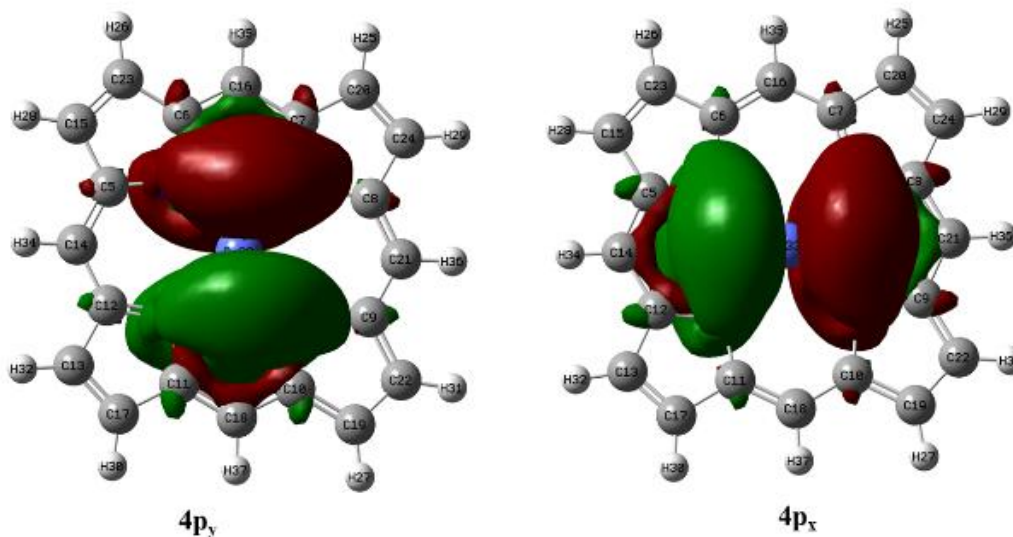


Figure S2. Co 4py- and 4px orbitals in complex 1.

Second-order perturbation analysis

Table S1

Second-order perturbation analysis of the Fock matrix in the NBO basis for complex 1 (α spin).				
Donor NBO (i)	Acceptor NBO (j)	$E(2)$ kcal/mol	$E(j)-E(i)$ a.u.	$F(i,j)$ a.u.
LP (N)(sp ²)	LP (Co)(d _{xy})	34.02	0.29	0.144
LP (N) (sp ²)	LP*(Co)(4s)	25.31	0.71	0.173
LP (N) (sp ²)	LP* (Co)(4p _y)	9.73	0.81	0.119
LP (N) (sp ²)	LP* (Co) (4p _x)	9.73	0.81	0.119

Table S2

Second-order perturbation analysis of the Fock matrix in the NBO basis for complex 2.				
Donor NBO (i)	Acceptor NBO (j)	$E(2)$ kcal/mol	$E(j)-E(i)$ a.u.	$F(i,j)$ a.u.
LP (N)(sp ²)	LP* (Co)(d _{xy})	65.22	0.31	0.140
LP (N) (sp ²)	LP*(Co)(4s)	49.60	0.87	0.189
LP (N) (sp ²)	LP* (Co)(4p _y)	24.93	0.81	0.134
LP (N) (sp ²)	LP* (Co) (4p _x)	26.84	0.82	0.139
σ (O38–C39)	LP* (Co) (4p _z)	13.20	1.09	0.110
σ (C39–H41)	σ^* (Co– O38)	8.79	0.60	0.068
LP* (Co)	σ^* (O38–C39)	8.32	0.05	0.050
LP (O38)	LP* (Co)	7.39	0.67	0.064
LP (O38)	σ^* (C39–H40)	11.30	0.79	0.085
LP (O38)	σ^* (C39–H42)	11.31	0.79	0.085
LP (O38)	LP* (Co)	20.35	1.10	0.141
LP (O38)	LP* (Co)	35.30	0.89	0.161
σ^* (Co– O38)	LP* (Co)	36.45	0.37	0.211
σ^* (Co– O38)	LP* (Co)	19.46	0.16	0.123

Table S3

Second-order perturbation analysis of the Fock matrix in the NBO basis for complex 3 (α -spin).				
Donor NBO (i)	Acceptor NBO (j)	$E(2)$ kcal/mol	$E(j)-E(i)$ a.u.	$F(i,j)$ a.u.
LP (N)(sp ²)	LP* (Co)(d _{xy})	28.20	0.37	0.140
LP (N) (sp ²)	LP*(Co)(4s)	19.48	0.83	0.163
LP (N) (sp ²)	LP* (Co)(4p _y)	11.12	0.79	0.123
LP (N) (sp ²)	LP* (Co) (4p _x)	11.89	0.80	0.128
σ (O38–C39)	LP* (Co) (4p _z)	4.92	1.11	0.097
σ (C39–H40)	LP* (Co)	0.34	0.56	0.019
LP* (Co)	σ^* (O38–C39)	1.24	0.19	0.055
LP (O38)	LP* (Co)	11.11	0.76	0.119
LP (O38)	σ^* (C39–H41)	7.80	0.71	0.095
LP (O38)	σ^* (C39–H42)	7.80	0.71	0.095
LP (O38)	LP* (Co)	13.41	0.83	0.137
LP (O38)	LP* (Co)	36.06	0.73	0.205
LP* (Co)	LP* (Co)	18.10	0.11	0.127

Table S4

Second-order perturbation analysis of the Fock matrix in the NBO basis for complex 4.				
Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
LP (N)(sp ²)	LP (Co)(d _{x²-y²})	69.52	0.33	0.148
LP (N) (sp ²)	LP*(Co)(4s)	52.68	0.90	0.197
LP (N) (sp ²)	LP* (Co)(4p _y)	48.77	0.80	0.186
σ (N-C)	LP* (Co)(4p _y)	8.44	1.22	0.094
σ (N-C)	LP* (Co) (4p _x)	8.44	1.22	0.094
σ* (Co-H)	LP* (Co) (4s)	237.62	0.16	0.366

Table S5

Second-Order Perturbation Analysis of the Fock Matrix in the NBO Basis for Complex 5 (β Spin).				
Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
LP (N)(sp ²)	LP (Co)(d _{x²-y²})	35.66	0.32	0.148
LP (N) (sp ²)	LP*(Co)(4s)	25.87	0.87	0.193
LP (N) (sp ²)	LP* (Co)(4p _y)	24.46	0.78	0.184
σ (N-C)	LP* (Co)(4p _y)	4.08	1.20	0.092
σ (N-C)	LP* (Co) (4p _x)	4.11	1.20	0.092
σ* (Co-H)	LP* (Co) (4s)	120.97	0.15	0.359
LP* (Co) (4p _y)	σ* (Co-H)	64.75	0.06	0.218

Cartesian coordinates and thermodynamic parameters

Cartesian coordinates and thermodynamic parameters calculated at the ωB97X-D/def2-TZVPP level of theory in the gas phase.
All Cartesian coordinates are given in Å.

Table S6

Cartesian coordinates of complex 1 (charge = 0, spin state: doublet, S = 1/2).			
Atom	X (Å)	Y (Å)	Z (Å)
N1	1.39382391	1.39382342	0.00000000
N2	-1.39382424	-1.39382329	0.00000000
N3	1.39382391	-1.39382331	0.00000000
N4	-1.39382408	1.39382415	0.00000000
C5	-2.74865129	1.21394894	0.00000000
C6	-1.21394939	2.74865084	0.00000000
C7	1.21394798	2.74865550	0.00000000
C8	2.74864612	1.21394753	0.00000000
C9	2.74865068	-1.21394699	0.00000000
C10	1.21394761	-2.74865191	0.00000000
C11	-1.21394743	-2.74864469	0.00000000
C12	-2.74865715	-1.21394868	0.00000000
C13	-3.42859366	-2.47559669	0.00000000
C14	-3.39217584	-0.00000131	0.00000000
C15	-3.42859350	2.47559228	0.00000000
C16	0.00000151	3.39217521	0.00000000
C17	-2.47559135	-3.42859343	0.00000000
C18	0.00000190	-3.39217399	0.00000000
C19	2.47559678	-3.42859395	0.00000000
C20	2.47559612	3.42859379	0.00000000

C21	3.39217475	-0.00000115	0.00000000
C22	3.42859438	-2.47559565	0.00000000
C23	-2.47559270	3.42859317	0.00000000
C24	3.42859346	2.47559288	0.00000000
H25	2.59136855	4.50025964	0.00000000
H26	-2.59136505	4.50025886	0.00000000
H27	2.59136702	-4.50025996	0.00000000
H28	-4.50025920	2.59136461	0.00000000
H29	4.50025960	2.59136033	0.00000000
H30	-2.59135831	-4.50025960	0.00000000
H31	4.50026045	-2.59136492	0.00000000
H32	-4.50025933	-2.59137083	0.00000000
Co33	0.00000009	-0.00000043	0.00000000
H34	-4.47303472	0.00000276	0.00000000
H35	-0.00000159	4.47303403	0.00000000
H36	4.47303300	0.00000194	0.00000000
H37	-0.00000307	-4.47303231	0.00000000

Table S7

Cartesian coordinates of complex 2 (charge = 0, spin state: singlet, S = 0).			
Atom	X (Å)	Y (Å)	Z (Å)
N1	1.34013899	-1.39321264	-0.27323369
N2	-1.44643213	1.39520442	-0.20343001
N3	-1.44534776	-1.39629697	-0.20333069
N4	1.33909425	1.39426355	-0.27317359
C5	1.16041195	2.74570648	-0.19501785
C6	2.69095657	1.21578993	-0.35392553
C7	2.69186528	-1.21370031	-0.35402956
C8	1.16250292	-2.74480498	-0.19519120
C9	-1.26498978	-2.74655781	-0.13488726
C10	-2.79679909	-1.21568570	-0.20153211
C11	-2.79774188	1.21356114	-0.20166371
C12	-1.26709657	2.74559771	-0.13496329
C13	-2.52921310	3.42685005	-0.10912070
C14	-0.05267413	3.38737085	-0.11370965
C15	2.41983536	3.42732005	-0.23893950
C16	3.33278675	0.00128751	-0.40036809
C17	-3.48126821	2.47423724	-0.15788475
C18	-3.44026968	-0.00131125	-0.21149927
C19	-3.47936470	-2.47687841	-0.15768692
C20	3.37272973	-2.47403865	-0.34568692
C21	-0.05007929	-3.38740625	-0.11378516
C22	-2.52658400	-3.42876800	-0.10895979
C23	3.37085536	2.47665136	-0.34542145
C24	2.42244394	-3.42544591	-0.23924693

H25	4.44233329	-2.59187121	-0.40974818
H26	4.44037194	2.59530658	-0.40941686
H27	-4.55111530	-2.59273148	-0.15850567
H28	2.53711948	4.49819213	-0.19990119
H29	2.54055143	-4.49623143	-0.20031443
H30	-4.55310686	2.58927305	-0.15875098
H31	-2.64251615	-4.49955572	-0.06368928
H32	-2.64596091	4.49754958	-0.06386230
Co33	-0.04441647	0.00002180	-0.06855965
H34	-0.05065214	4.46664173	-0.05314563
H35	4.41225785	0.00169188	-0.45725151
H36	-0.04722388	-4.46667860	-0.05327733
H37	-4.52123666	-0.00173129	-0.20421894
O38	-0.11103725	0.00026610	1.73902578
C39	1.07013166	-0.00007687	2.46769230
H40	1.69177456	0.88845319	2.29648875
H41	0.78109623	0.00026432	3.52477609
H42	1.69104170	-0.88918766	2.29686147

Table S8

Cartesian coordinates of complex 3 (charge = -1, spin state: doublet, S = 1/2).			
Atom	X (Å)	Y (Å)	Z (Å)
N1	-1.35711473	1.40849113	-0.27598698
N2	1.46709739	-1.40894151	-0.19350138
N3	-1.35578005	-1.40971987	-0.27606837
N4	1.46575794	1.41031920	-0.19333279
C5	2.81005083	1.22492358	-0.17705696
C6	1.27661160	2.75418836	-0.17475196
C7	-1.17050468	2.75323362	-0.24477382
C8	-2.70088720	1.22233032	-0.34573265
C9	-2.69972255	-1.22482055	-0.34575225
C10	-1.16790490	-2.75427601	-0.24487356
C11	1.27920439	-2.75297007	-0.17492688
C12	2.81120428	-1.22228701	-0.17714797
C13	3.49902917	-2.48824123	-0.15530746
C14	3.44882201	0.00162009	-0.17036316
C15	3.49668590	2.49151863	-0.15522814
C16	0.05230028	3.39059462	-0.18710553
C17	2.54453574	-3.44180897	-0.15107155
C18	0.05548770	-3.39050969	-0.18730023
C19	-2.43127957	-3.44342879	-0.29730616
C20	-2.43452548	3.44119679	-0.29726132
C21	-3.33742258	-0.00154615	-0.37927166
C22	-3.38512274	-2.49094676	-0.36339775

C23	2.54130340	3.44420099	-0.15093845
C24	-3.38746918	2.48781124	-0.36340427
H25	-2.55277046	4.51368945	-0.28343729
H26	2.65745884	4.51686778	-0.13174445
H27	-2.54851307	-4.51602930	-0.28347977
H28	4.56908193	2.61063727	-0.13897984
H29	-4.45882791	2.60641634	-0.41285415
H30	2.66169132	-4.51436359	-0.13186969
H31	-4.45637265	-2.61055623	-0.41279208
H32	4.57153540	-2.60635751	-0.13899794
Co33	0.05066661	0.00003199	-0.08450835
H34	4.53114572	0.00213294	-0.15130829
H35	0.05095821	4.47283321	-0.16381724
H36	-4.41874257	-0.00205980	-0.42687278
H37	0.05514388	-4.47274173	-0.16403086
O38	0.08830460	-0.00033691	1.95615647
C39	-1.08170670	-0.00047076	2.64430101
H40	-0.92009637	-0.00058192	3.74370113
H41	-1.73394686	-0.88402226	2.44650811
H42	-1.73404298	0.88305071	2.44669984

Table S9

Cartesian coordinates of complex 4 (charge = 0, spin state: singlet, S = 0).

Atom	X (Å)	Y (Å)	Z (Å)
N1	0.00004414	1.96912225	-0.02537947
N2	-0.00004446	-1.96912184	-0.02537891
N3	1.96907463	-0.00004411	-0.02601830
N4	-1.96907443	0.00004448	-0.02601796
C5	-2.80105754	-1.08385241	-0.01854915
C6	-2.80100906	1.08397856	-0.01854960
C7	-1.08375955	2.80104592	-0.01683988
C8	1.08388535	2.80099718	-0.01683915
C9	2.80105782	1.08385260	-0.01854913
C10	2.80100886	-1.08397845	-0.01854968
C11	1.08375938	-2.80104571	-0.01683935
C12	-1.08388560	-2.80099702	-0.01683908
C13	-0.67409070	-4.17516904	-0.01514210
C14	-2.39756625	-2.39744849	-0.01284476
C15	-4.17524816	-0.67385244	-0.01895004
C16	-2.39745850	2.39755653	-0.01284571
C17	0.67390272	-4.17519930	-0.01514224
C18	2.39745819	-2.39755634	-0.01284540
C19	4.17521791	-0.67404022	-0.01895009
C20	-0.67390295	4.17519962	-0.01514235
C21	2.39756612	2.39744871	-0.01284463

C22	4.17524832	0.67385232	-0.01894936
C23	-4.17521800	0.67404008	-0.01895006
C24	0.67409050	4.17516931	-0.01514179
H25	-1.34986665	5.01498937	-0.01513670
H26	-5.01541841	1.34951871	-0.02010988
H27	5.01541827	-1.34951893	-0.02010998
H28	-5.01547887	-1.34929339	-0.02010982
H29	1.35009197	5.01492865	-0.01513559
H30	1.34986631	-5.01498913	-0.01513668
H31	5.01547913	1.34929314	-0.02010858
H32	-1.35009206	-5.01492849	-0.01513640
Co33	0.00000024	-0.00000056	0.05182126
H34	-3.16189160	-3.16198650	-0.00601512
H35	-3.16174927	3.16212911	-0.00601623
H36	3.16189123	3.16198694	-0.00601446
H37	3.16174901	-3.16212886	-0.00601588
H38	0.00000206	0.00000074	1.46125502

Table S10

Cartesian coordinates of complex 5 (charge = -1, spin state: doublet, S = 1/2).

Atom	X (Å)	Y (Å)	Z (Å)
N1	1.97545894	0.00000061	-0.03115453
N2	-1.97545868	0.00000053	-0.03115226
N3	-0.00000069	-1.99006985	-0.02183892
N4	-0.00000082	1.99006982	-0.02183803
C5	-1.08760278	2.82493984	-0.01750907
C6	1.08760158	2.82493973	-0.01750911
C7	2.80768292	1.09387130	-0.02055247
C8	2.80768284	-1.09387038	-0.02055112
C9	1.08760225	-2.82493976	-0.01750882
C10	-1.08760317	-2.82493994	-0.01751013
C11	-2.80768272	-1.09386990	-0.02055080
C12	-2.80768281	1.09387049	-0.02055082
C13	-4.18992338	0.67107169	-0.01962528
C14	-2.42053948	2.39686122	-0.01349950
C15	-0.68699518	4.17685011	-0.02028066
C16	2.42053838	2.39686185	-0.01350032
C17	-4.18992333	-0.67107048	-0.01962513
C18	-2.42053984	-2.39686059	-0.01350020
C19	-0.68699527	-4.17684971	-0.02028084
C20	4.18992311	0.67107206	-0.01962569
C21	2.42053899	-2.39686101	-0.01349871
C22	0.68699366	-4.17684953	-0.02027945
C23	0.68699323	4.17684998	-0.02028031
C24	4.18992307	-0.67107050	-0.01962461

H25	5.03108921	1.34735735	-0.01967657
H26	1.36145126	5.01912347	-0.02370326
H27	-1.36145323	-5.01912326	-0.02370409
H28	-1.36145357	5.01912337	-0.02370391
H29	5.03108942	-1.34735544	-0.01967440
H30	-5.03108942	-1.34735578	-0.01967614
H31	1.36145130	-5.01912328	-0.02370149
H32	-5.03108924	1.34735733	-0.01967647
Co33	0.00000208	-0.00000168	0.06159513
H34	-3.19075357	3.15682979	-0.00674908
H35	3.19075167	3.15683125	-0.00674932
H36	3.19075288	-3.15682981	-0.00674642
H37	-3.19075440	-3.15682871	-0.00674953
H38	0.00000798	-0.00000770	1.47450668

Table S11

Thermodynamic parameters of complexes 1–5.

Parameter	Complex 1	Complex 2	Complex 3	Complex 4	Complex 5
Zero-point correction	0.278370	0.321111	0.315781	0.286866	0.282675
Thermal correction to Energy	0.295253	0.341069	0.336682	0.303848	0.300100
Thermal correction to Enthalpy	0.296197	0.342013	0.337626	0.304792	0.301044
Thermal correction to Gibbs Free Energy	0.232934	0.273673	0.264428	0.242990	0.237760
Sum of electronic and zero-point Energies	-2370.948618	-2486.055777	-2486.129725	-2371.555640	-2371.605820
Sum of electronic and thermal Energies	-2370.931736	-2486.035819	-2486.108824	-2371.538657	-2371.588396
Sum of electronic and thermal Enthalpies	-2370.930792	-2486.034875	-2486.107880	-2371.537713	-2371.587451
Sum of electronic and thermal Free Energies	-2370.994055	-2486.103215	-2486.181077	-2371.599516	-2371.650735

All energies are given in hartree.

The Gibbs free energy (G) at 298.15 K and 1 atm in the gas phase corresponds to the sum of electronic and thermal free energies.