Supporting Information

Methylene bridge regulated geometrical preferences of ligands in cobalt(III) coordination chemistry and phenoxazinone synthase mimicking activity

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Content

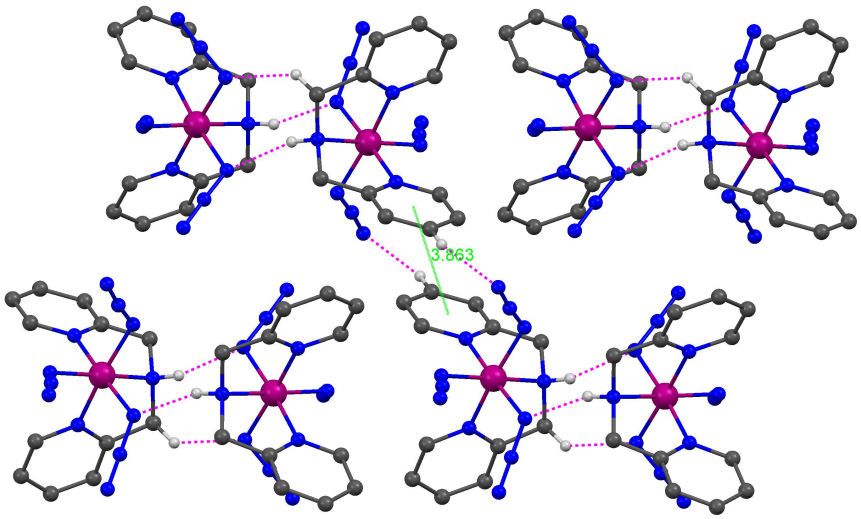


Fig. S1. Packing diagram of complex *fac*-**1** showing hydrogen bonding and π–π stacking interaction. Hydrogen atoms not involved in hydrogen bonding are omitted for clarity.

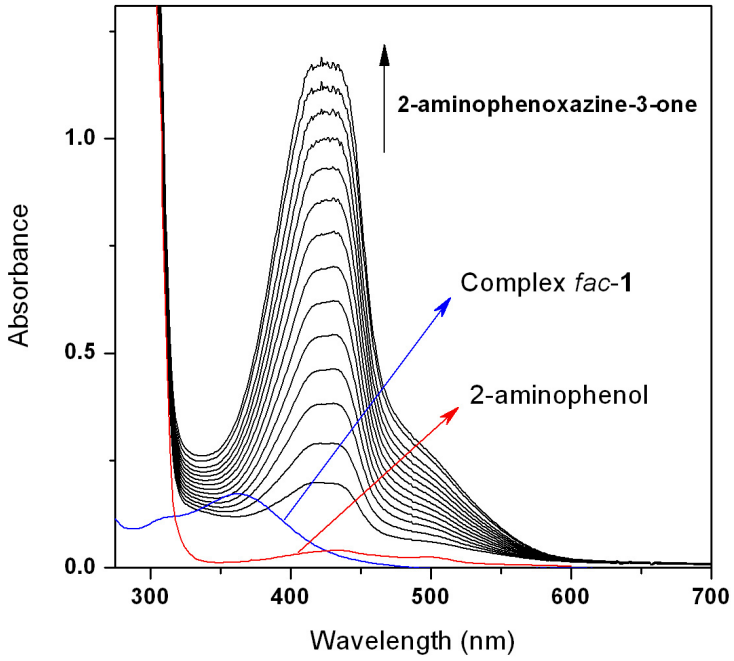


Fig. S2. The spectral profile showing the growth of 2-aminophenoxazine-3-one at 433 nm after addition of 0.01 M *o*-aminophenol to a solution containing complex *fac*-**1** (2 x 10^{-5} M) in MeCN. The spectra were recorded for the period of 2 h in aerobic condition at 25 °C.

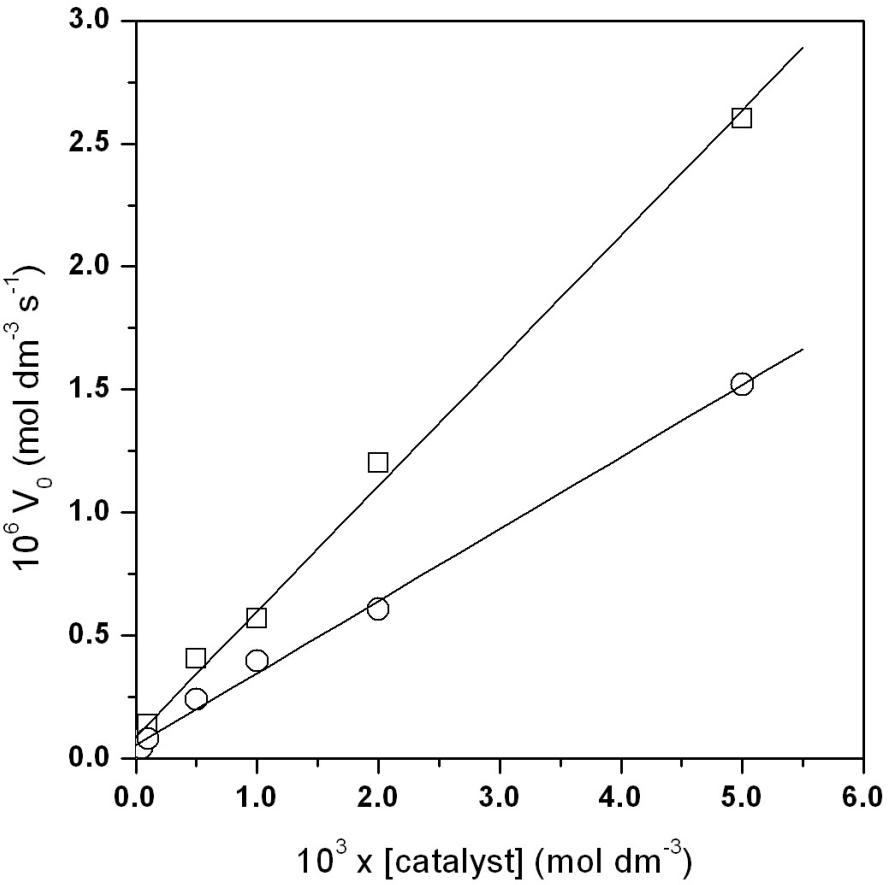


Fig. S3. Plot of initial rates on the complex concentrations for the oxidation of *o*-aminophenol catalyzed by the complexes in dioxygen-saturated methanol at 25 ºC

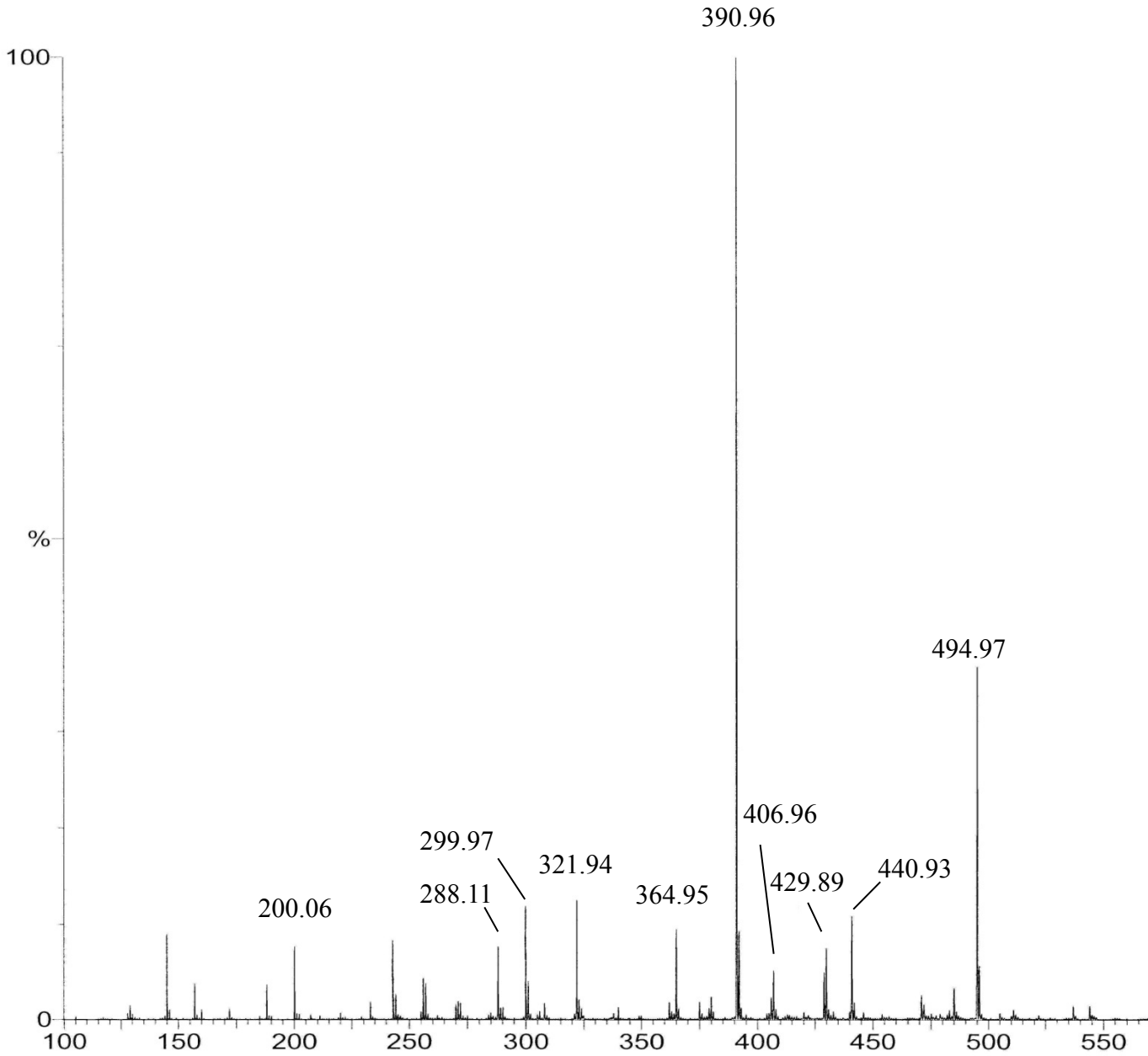


Fig. S4. Electrospray ionization mass spectrum (ESI-MS positive) of $[Co(L^1)(N_3)_3]$ (*fac*-**1**) in methanol.

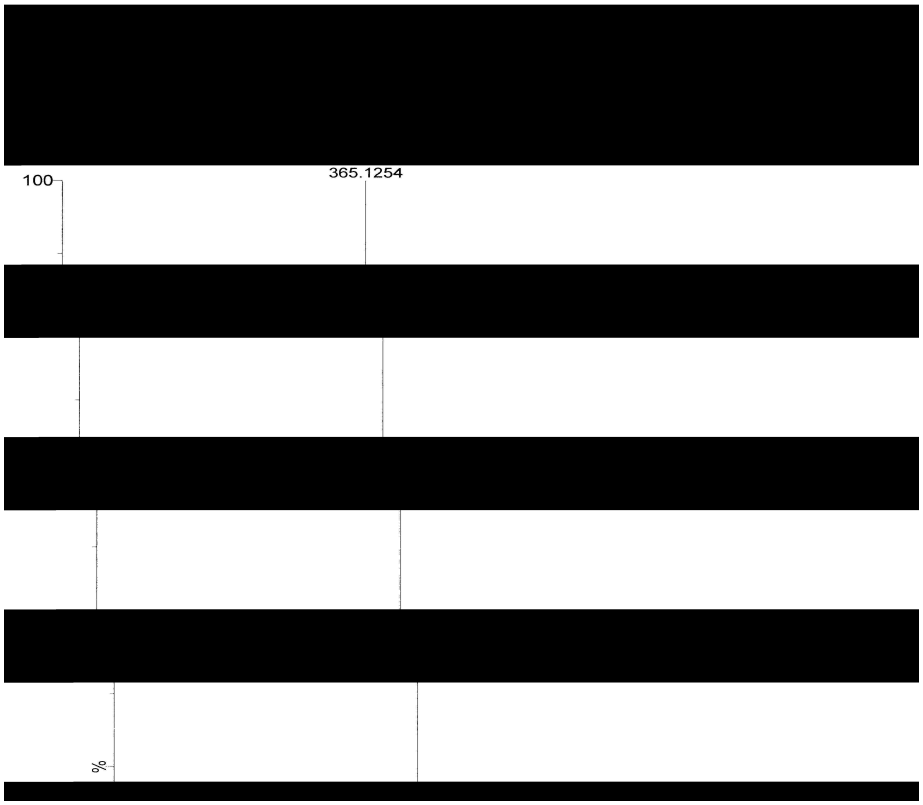
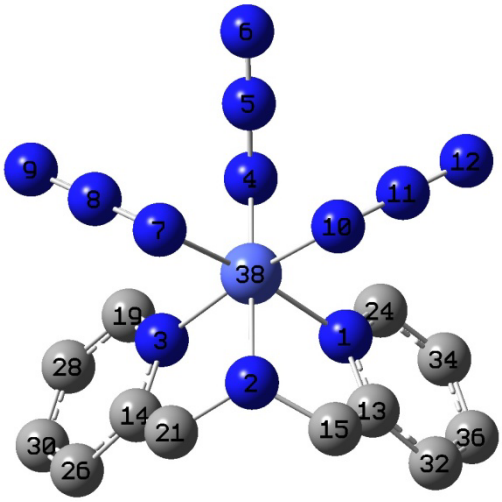
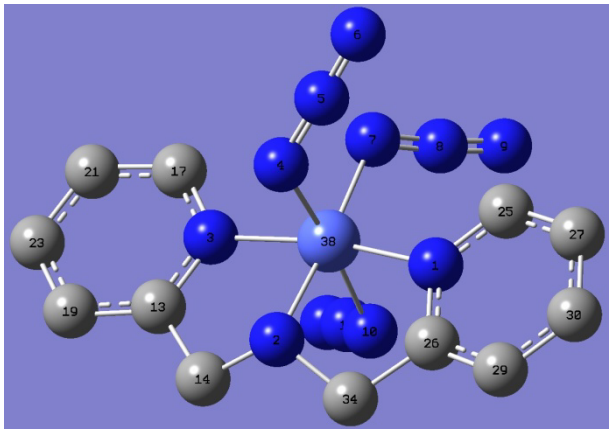


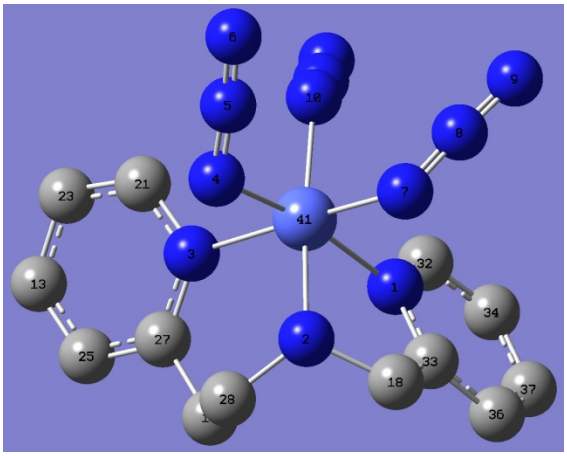
Fig. S5. Electrospray ionization mass spectrum (ESI-MS positive) of a 1:50 mixture of $[Co(L^1)(N_3)_3]$ (*fac*-**1**) and *o*-aminophenol in methanol recorded after 5 min of mixing.



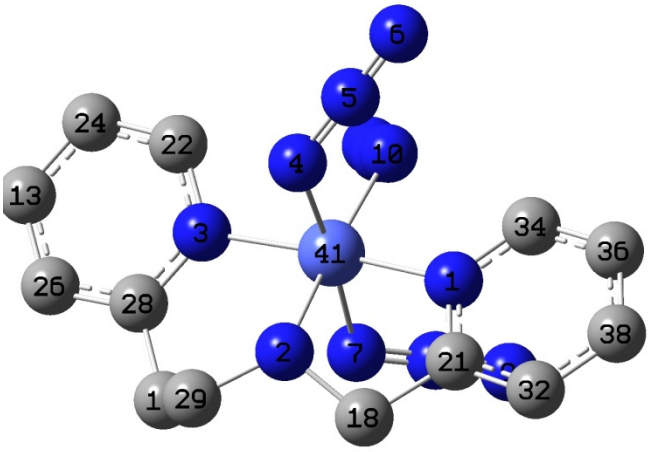
L^1_facial



L^1_meridional



L^2_facial



L^2_meridional

Fig. S6. DFT optimized structures of both facial and meridional isomers of **1** and **2**; Hydrogen atom is removed for clarity.

Table S1. Cartesian Coordinates for Ground State Optimized Structures and their Energies in Hartrees; Gas Phase Calculations: B3LYP/6-31+g(d) for H,C,N and LANL2DZ for Co

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$[Co(L^2)(N_3)_3]$ (*mer*):

Atom	Coordinates (Angstroms) X	Y	Z
N	1.94713000	-0.02206900	-0.11695100
N	0.19646800	1.82720200	-0.79926500
N	-2.01925800	0.01560100	-0.18892800
N	-0.03958600	-0.52263300	-2.06967700
N	0.56430800	-1.50557900	-2.45143000
N	1.12641200	-2.42770200	-2.86496800
N	-0.04398000	0.55940300	1.76202400
N	0.77126800	0.11826700	2.54902100
N	1.52955600	-0.25252300	3.33963000
N	-0.00510000	-1.95950900	0.39065200
N	-0.64601700	-2.34350600	1.35287600
N	-1.24596900	-2.79295400	2.23128000
C	-4.80366900	-0.01395400	-0.24047600
H	-5.89028000	-0.02082000	-0.24384800
C	-1.93934100	2.40662600	0.40820600
H	-1.40073300	2.29634900	1.35473600
H	-2.65090000	3.23297900	0.51332600
C	1.44836700	2.33599800	-0.20393800
H	1.22584000	2.63230000	0.82741500
H	1.82557400	3.21451600	-0.74530000
C	2.46632900	1.22240200	-0.19449200
C	-2.69045400	-1.09306600	-0.55469900
H	-2.07564000	-1.94452700	-0.81815500
C	-4.07920200	-1.15271800	-0.58751100
H	-4.56864600	-2.07701700	-0.87585900
C	-4.10597500	1.14305800	0.09852900
H	-4.63571400	2.05640600	0.35159900
C	-2.70618800	1.14116500	0.11320100
C	-0.95154900	2.76524500	-0.71334600
H	-1.46626500	2.74959600	-1.67958200
H	-0.57720300	3.78544600	-0.55782200
C	3.84194600	1.43172800	-0.23363500
H	4.23470300	2.44175200	-0.30376400
C	2.75947500	-1.08928000	-0.06407100
H	2.26212200	-2.05039300	0.00479000
C	4.14635700	-0.95041300	-0.09242200
H	4.77204000	-1.83558400	-0.05011400
C	4.69569200	0.32701200	-0.17796100
H	5.77279100	0.46628500	-0.20411300
H	0.35882900	1.57387400	-1.77706400
Co	-0.02310600	-0.08229500	-0.11408900

Energy: -1306.435902 Hartrees

$[Co(L^2)(N_3)_3]$ (*fac*):

Atom	Coordinates (Angstroms) X	Y	Z
N	-1.28965900	-0.86191100	0.38389500
N	-0.36708100	-0.30314800	-2.07038500
N	1.70288900	-0.40776700	0.11630600
N	1.08898300	1.86153400	-1.29305400
N	0.93717200	3.06194400	-1.13468800
N	0.86618000	4.20772400	-1.03993500
N	-1.65255200	1.63378300	-0.85890700
N	-2.33479700	2.20037900	-0.02328700
N	-3.04193300	2.75426000	0.69971700
N	0.06304900	1.72784200	1.31960800
N	0.14391800	1.29070300	2.44143900
N	0.24366300	0.93446800	3.54496600
C	4.11096900	-1.63398300	0.84095200
H	5.03761800	-2.12378100	1.12752600
C	1.17345800	-2.19147700	-1.50370600
H	0.29743500	-2.68315400	-1.06266900
H	1.73950600	-2.98002200	-2.01089700
C	-1.68970700	-0.96687800	-2.00843700
H	-1.75564200	-1.78777000	-2.73501300
H	-2.44235900	-0.21602400	-2.26438300
C	2.56879100	0.19460100	0.95574200
H	2.27604800	1.17703900	1.30161900
C	3.77135700	-0.38310100	1.35073100
H	4.41813000	0.14956500	2.03999300
C	3.24630800	-2.23240100	-0.07279400
H	3.49465100	-3.18647800	-0.52830600
C	2.05224600	-1.59450300	-0.42896000
C	0.73350400	-1.15919900	-2.55245500
H	1.56617300	-0.49533700	-2.80194900
H	0.42171300	-1.67784300	-3.47055200
H	-0.42647200	0.53480400	-2.64975000
C	-1.52704200	-1.23234200	1.65505400
C	-1.97617600	-1.46400100	-0.61173900
C	-2.46358100	-2.21016600	1.98529600
H	-0.95645200	-0.73317600	2.42901600
C	-2.92114900	-2.45847400	-0.35743700
C	-3.17549300	-2.83387600	0.96169300
H	-2.62277800	-2.46533300	3.02774600
H	-3.45027100	-2.92363100	-1.18441500
H	-3.91269500	-3.60048600	1.18359900
Co	-0.06016100	0.64102800	-0.30684900

Energy: -1306.420824 Hartrees

$[Co(L^1)(N_3)_3]$ (fac):

Atom	Coordinates (Angstroms) X	Y	Z
N	1.41658400	-0.64695100	-0.33078500
N	-0.00054300	-0.62626300	1.95238500
N	-1.41730300	-0.64544200	-0.33098300
N	0.00066700	1.62165000	-1.29741000
N	0.00229400	2.84403200	-1.26019000
N	0.00368400	3.99304700	-1.32062300
N	-1.37436400	1.65102500	1.26592100
N	-2.37429100	1.97080300	0.65203600
N	-3.35422600	2.30051200	0.13215700
N	1.37610000	1.64919800	1.26626600
N	2.37621400	1.96845500	0.65240900
N	3.35637700	2.29758200	0.13259500
C	1.82207200	-1.56282600	0.56962700
C	-1.82412500	-1.56063100	0.56950500
C	1.26199400	-1.39689600	1.96631000
H	-0.00005800	0.06584400	2.69930100
H	1.13565100	-2.36978400	2.45867900
H	1.98468400	-0.81731600	2.55070500
C	-1.94188000	-0.63803800	-1.56600700
H	-1.57188200	0.14830300	-2.21700200
C	-1.26415200	-1.39512500	1.96627000
H	-1.13927700	-2.36806200	2.45892400
H	-1.98614200	-0.81436800	2.55035700
C	1.94147000	-0.63994100	-1.56566700
H	1.57253300	0.14692300	-2.21663600
C	-2.76505000	-2.53585500	0.23953000
H	-3.07192600	-3.26826000	0.98086300
C	-2.89813700	-1.57144700	-1.96131600
H	-3.30771300	-1.53058900	-2.96529900
C	-3.31031000	-2.54024800	-1.04586400
H	-4.05011800	-3.28572300	-1.32403000
C	2.76186500	-2.53913000	0.23967600
H	3.06767700	-3.27207000	0.98092000
C	2.89670200	-1.57443600	-1.96093900
H	3.30657700	-1.53383900	-2.96481100
C	3.30744900	-2.54392600	-1.04559600
H	4.04640100	-3.29026700	-1.32371800
Co	0.00029100	0.61246900	0.34452300

Energy: -1267.114047 Hartrees

$[Co(L^1)(N_3)_3]$ (mer):

Atom	Coordinates (Angstroms) X	Y	Z
N	1.92678800	-0.19968100	-0.05683300
N	-0.09837400	-1.88221500	0.19907200
N	-1.96032200	-0.00797700	0.27906800
N	0.12499400	-0.00974100	2.08645200
N	0.79247800	0.81712500	2.67434000
N	1.42152100	1.57518400	3.27992800
N	0.01493500	2.04357400	0.11325700
N	0.53809500	2.65720600	-0.79999500
N	1.03450700	3.31408200	-1.61099500
N	-0.13843300	-0.06498700	-1.88167900
N	-1.03718200	0.50843300	-2.46708500
N	-1.87512000	1.02067100	-3.07790700
C	-2.44961100	-1.26056400	0.15987000
C	-1.43896100	-2.31586700	-0.24191600
H	-1.70917600	-3.30025600	0.16139100
H	-1.41710400	-2.38604000	-1.33486300
C	-2.77331900	1.01239100	0.58421700
H	-2.28842400	1.97969100	0.66530000
C	-3.80280400	-1.52673700	0.35566400
H	-4.17560400	-2.54279800	0.26516600
C	-4.14001100	0.81969500	0.77739900
H	-4.77311600	1.66760700	1.01688900
C	-4.66114500	-0.46870500	0.66422900
H	-5.72104400	-0.65199200	0.81691200
C	2.90073300	0.70302500	0.13055100
C	2.24112200	-1.48815300	-0.32121100
C	4.24817100	0.35742600	0.04153500
H	2.58157800	1.71108800	0.36545000
C	3.56686000	-1.90447900	-0.41225900
C	4.58618700	-0.96545700	-0.23692800
H	5.00607200	1.11777200	0.19676900
H	3.79452400	-2.94666200	-0.61620300
H	5.62721800	-1.26786800	-0.30742000
C	1.06448500	-2.41722700	-0.53648700
H	0.80568600	-2.41229000	-1.60028000
H	1.30909400	-3.44450200	-0.23697400
H	0.01441000	-2.00408500	1.20928800
Co	-0.01153900	0.10394500	0.09063800

Energy: -1267.120315 Hartrees

Table S2: Comparison of Bond distance (Å) and angle (˚) of crystal structure and calculated values of their facial and meridional conformations.

	Complex **1**			Complex **2**		
	Crystal	Calculated(DFT)		Crystal	Calculated(DFT)	
	(Facial)[#]	Facial	Meridional	(Meridional)	Meridional	Facial
Bond						
Co1-N1	1.950	2.01	1.96	1.929	1.97	2.06
Co1-N2	1.960	2.03	1.99	1.964	2.04	2.023
Co1-N3	1.941	2.01	1.96	1.969	1.999	2.095
Co1-N4	1.935	1.92	2.00	1.978	2.00	1.945
Co1-N7	1.936	1.95	1.94	1.971	1.98	1.956
Co1-N10	1.955	1.95	1.98	1.949	1.94	1.96
Angle						
N1–Co1–N2	84.7	83.34	83.86	81.7	82.147	82.03
N2–Co1–N3	84.2	83.34	83.94	93.9	92.81	94.02
N1–Co1–N3	87.3	89.54	167.8	175.7	174.92	93.97
N1–Co1–N7	174.4	170.5	98.15	90.9	90.774	88.8
N2–Co1–N10	88.7	87.16	88.07	171.9	171.82	172.45
N2–Co1–N4	176.4	173.96	83.8	85.7	90.917	86.59
N3–Co1–N10	172.8	170.49	91.55	93.8	93.797	93.27
N4–Co1–N7	92.4	97.09	92.53	176.3	173.71	91.11
N6–N5–N4	174.9	175.24	177.28	176.6	177.35	175.44
N9–N8–N7	178.7	176.29	175.38	175.3	176.69	175.37
N10–N11–N12	175.6	176.29	176.75	176.6	175.42	176.45

[#] Average value of two crystallographically independent molecules