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Dioxygen bound Cobalt Corroles

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METHODS

Materials. The complexes are synthesized as previously reported. Sodium borohydride and cobaltocene were purchased from Rankem and Sigma-Aldrich respectively.$^{18}O_2$ was obtained from Icon Isotopes. Solvents are purchased from Merck (HPLC grade) and purified and dried by passing through an activated alumina purification system (MBraun SPS) and stored in an anaerobic glove box maintained in Argon atmosphere.

EPR specrtroscopy. All the electron paramagnetic resonance (EPR) spectra were recorded on a JEOL instrument. The EPR spectra were measured at 77 *K*. The EPR signal due to CoCorrole oxy vanishes with a ~ $t_{1/2}$<60s while warming up to room temperature.

Resonance Raman spectroscopy. Resonance Raman (rR) data were collected using 413.1 nm excitation from a Kr+ ion source (Coherent Inc.) and a Trivista 555 triple spectrophotometer (gratings used in the three stages were 900, 900, and 1800 grooves/mm) fitted with an electronically cooled Pixis CCD camera (Princeton Instruments). The irradiation power was limited to 10 mW at the sample to avoid degradation. Data were collected at room temperature and 77 K for 200 s.

Experimental Details. A 1.167 mg portion of $CoCl_8$ catalyst was dissolved in 1 mL of dry degassed tetrahydrofuran (THF) solvent so that the final strength was 1 mM. A 2.4 mg portion of $NaBH_4$ was dissolved in minimum volume of methanol and diluted with dry, degassed THF to make the final volume 1 mL, so that the final strength was 10 mM. Next 200 µL of this 1 mM $CoCl_8$ solution was taken in two EPR tubes. To both EPR tubes, 1 equiv (20 µL) of $NaBH_4$ solution was added at room temperature. Dry oxygen was then added to one of the EPR tubes at -80°C. EPR and rR of both the samples were recorded. The corresponding $^{18}O_2$ adducts were prepared by adding dry $^{18}O_2$ to the reduced $CoCl_8$ samples at -80°C. The oxy adduct of Co-H_8 was prepared using the same procedure

Computational Details. All calculations were performed at the IACS computer cluster using Gaussian 03 software BP86 functional were used and a mixed basis set with 6-311 g* on the Co atom and 6-31g* on the C, N, F, Cl and H atoms were used for optimization. Frequency calculations were performed using the basis set used for optimization, and no negative frequencies were found for the structures reported.

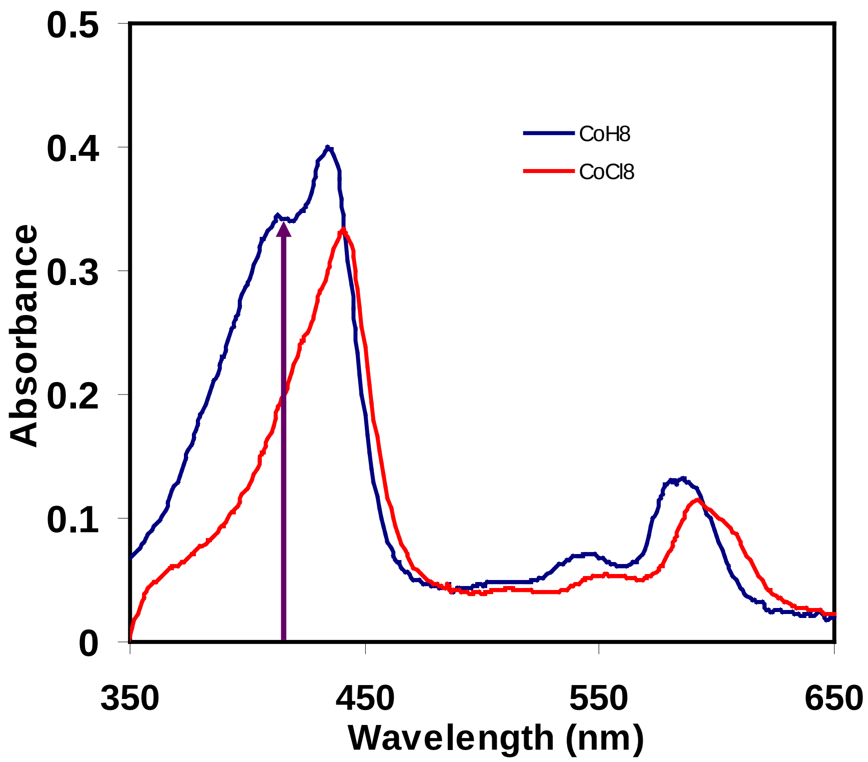

Figure s1. Absorption spectra of Co-H_8 (blue) and Co-Cl_8 (red). Purple line showing 413 nm where the laser excitation was made for resonance Raman spectroscopy.

Table S1. Experimental and theoretical stretching frequencies of Co-O_2 of Cobalt corrole in cm^{-1}

	CoH_8		$CoCl_8$	
	Experimental	DFT (scaled by 0.95)	Experimental	DFT (scaled by 0.95)
Co-O	547	514	509	498
O-O	1138	1153	1146	1163

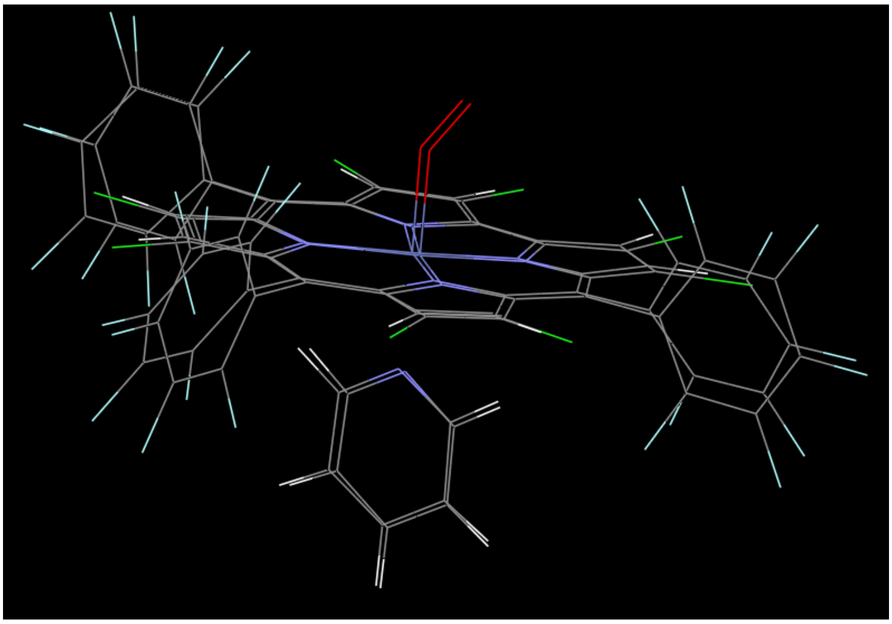

Figure s2. Overlay of the optimized geometry of the oxy adduct of CoH_8 and $CoCl_8$.

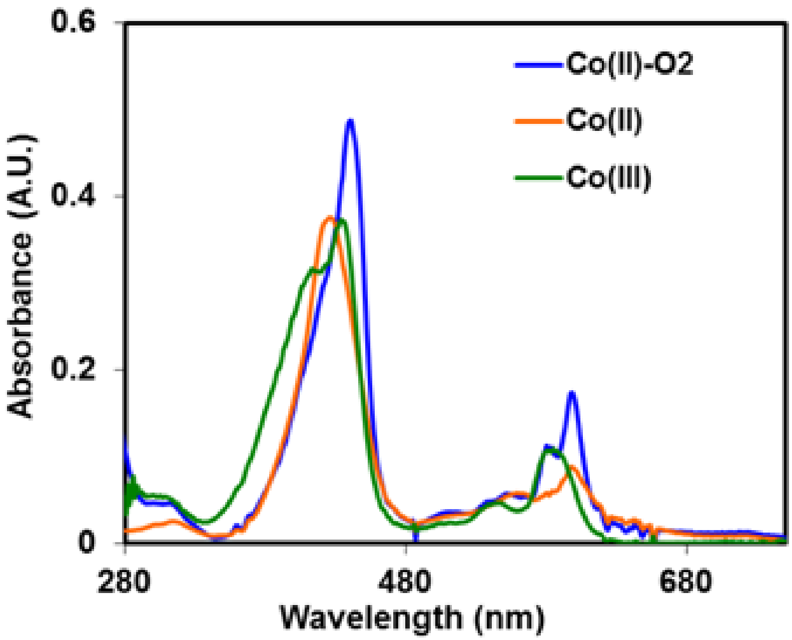

Figure s3. Absorption spectra of Co(III)-H_8 (green), Co(II)-H_8 (orange) and oxy adduct of Co-H_8 (blue; measured at -80^{0}C) .

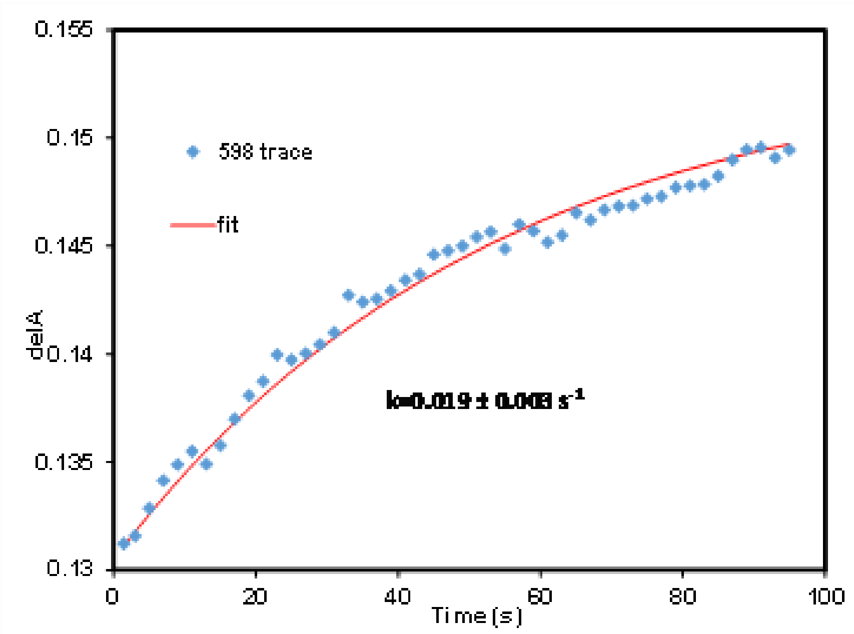

Figure s4. Kinetics of oxygen binding of the Co-H_8 complex at -80^{0}C. The data shows a decay constant of 0.019±0.003 s^{-1}.

Coordinates of Optimised Geometries

1.$CoCl_8$-O_2

Co	14.04681100	4.74871700	11.21426400
N	12.70865100	5.41539200	10.05640900
N	15.43894200	5.45870000	10.07432500
N	15.23067900	4.00406500	12.55163800
N	12.53058800	4.16542300	12.18134100
C	11.40160400	5.18039500	10.41989000
C	10.55467200	5.78023200	9.43492800
C	11.38588500	6.38130100	8.49045900
C	12.75917200	6.15160700	8.89852800
C	13.99556900	6.53606300	8.32430700

C	15.24728900	6.20020700	8.90544300
C	16.56272100	6.52261800	8.38406600
C	17.50516000	5.98028200	9.23165000
C	16.79495900	5.31365800	10.31424600
C	17.35741300	4.64762000	11.43390300
C	16.61296200	4.05553500	12.48671000
C	17.13259900	3.40835000	13.68338400
C	16.05482600	2.99608400	14.43765300
C	14.84186000	3.36765200	13.73323100
C	13.50690700	3.10528500	14.14026400
C	12.38316300	3.50494700	13.37608300
C	10.95700500	3.35119900	13.59442600
C	10.29529600	3.94470300	12.52016600
C	11.29922700	4.45902800	11.63981600
C	13.94835600	7.28188800	7.02948500
C	13.24597100	2.32647800	15.38919000
C	18.85067600	4.57661200	11.51731900
N	14.08000100	2.94211500	10.15678700
C	14.16489700	2.92526100	8.80408900
C	14.16673800	1.73993400	8.05854600
C	14.07559400	0.51210600	8.72827900
C	13.98218000	0.52457900	10.12670900
C	13.98690600	1.75254300	10.79983100

H	14.23814400	1.79387900	6.96772000
H	14.07499400	-0.43254800	8.17305500
H	13.90497800	-0.40183200	10.70433800
H	13.91242000	1.79165700	11.88892500
H	14.23138400	3.89623800	8.30805000
C	19.55994700	3.49337500	10.97096500
C	20.95689100	3.41179700	11.03909900
C	21.67589800	4.43725500	11.67003300
C	20.99677800	5.53149400	12.22578400
C	19.59940400	5.58873600	12.14341000
F	18.89656900	2.49056800	10.35822200
F	21.61651200	2.36018200	10.50607100
F	23.02142900	4.37101300	11.74231600
F	21.69592300	6.51536600	12.83097400
F	18.97615700	6.65312000	12.68390200
C	13.92235600	6.59395400	5.80445700
C	13.84443800	7.26360600	4.57694500
C	13.78313700	8.66480900	4.56308400
C	13.80163600	9.38067100	5.76910400
C	13.88021400	8.68528800	6.98370000
F	13.98254600	5.24274000	5.78689500
F	13.82620900	6.57936900	3.41263100
F	13.70734100	9.32346400	3.38859400

F	13.74179400	10.72883600	5.74707100
F	13.89664500	9.39943000	8.12424700
C	13.13900000	0.92592400	15.35050200
C	12.86050900	0.16867900	16.49534500
C	12.67608200	0.82350200	17.72182100
C	12.77166700	2.22114400	17.79279300
C	13.05125200	2.95460600	16.63150100
F	13.31201900	0.26637200	14.18194700
F	12.76760500	-1.17717100	16.43110900
F	12.40796000	0.10873200	18.83368200
F	12.59258700	2.84371300	18.97680700
F	13.13854400	4.29380000	16.73180100
O	14.13338700	6.39432700	12.18507200
O	13.05199300	7.02232200	12.46579800
Cl	10.78672800	7.24375000	7.10563100
Cl	16.99097400	7.42405900	6.96186300
Cl	19.21098700	6.13775900	8.93530400
Cl	18.77217800	3.14615600	14.19812900
Cl	16.23466300	2.18987300	15.96623700
Cl	10.13048700	2.59265800	14.92204300
Cl	8.57572900	4.01276200	12.33271700
Cl	8.82473200	5.78685100	9.37699100

2.CoH_8-O_2

Co	14.01539900	4.71714300	11.19367400
N	12.69238300	5.38558800	10.04151300
N	15.40110200	5.43445100	10.08244900
N	15.18973300	3.96192800	12.50530400
N	12.50969100	4.13194600	12.14954200
C	11.38207700	5.16972400	10.40225300
C	10.53479500	5.79820100	9.43149000
C	11.37174100	6.39996100	8.49261700
C	12.73533600	6.13451300	8.89503900
C	13.98218600	6.51733200	8.33157700
C	15.23295000	6.16963300	8.91382800
C	16.54061900	6.47486300	8.37447700
C	17.47760400	5.93651700	9.22837600
C	16.75530400	5.29614700	10.30769700
C	17.31674900	4.63109600	11.42867400
C	16.56764000	4.02746900	12.47201000
C	17.09507500	3.41447600	13.67289600
C	16.01880000	2.98516700	14.41766000
C	14.81812600	3.32720600	13.68656000
C	13.48052500	3.06137600	14.09298000

C	12.34915600	3.46940500	13.33752000
C	10.92923300	3.31308100	13.56490200
C	10.26673200	3.91873200	12.49825200
C	11.27639900	4.43337800	11.61981200
C	13.96977700	7.30083700	7.06638400
C	13.25558100	2.29536700	15.34873700
C	18.80382300	4.57725600	11.53015600
N	14.05064300	2.92844600	10.12397900
C	14.05120900	2.92868300	8.76857700
C	14.04549100	1.75150800	8.00955600
C	14.03564700	0.51385800	8.66785100
C	14.02901400	0.50946900	10.06966900
C	14.03572400	1.73001600	10.75679800
H	14.04752200	1.81807600	6.91666400
H	14.03148200	-0.42485400	8.10187900
H	14.01976900	-0.42587200	10.63871800
H	14.03480300	1.76101300	11.84897900
H	14.05121800	3.90912200	8.28614200
C	19.50991100	3.35857200	11.43867000
C	20.90736300	3.28900400	11.54323000
C	21.64841900	4.46413100	11.73111200
C	20.98336900	5.69510700	11.81971000
C	19.58336500	5.73760300	11.72787000

F	18.84655800	2.20221600	11.22896000
F	21.54844200	2.10214600	11.44318800
F	22.99505400	4.41014600	11.82515100
F	21.69571700	6.82762700	12.01412300
F	18.99161900	6.94203100	11.84824600
C	13.46840500	6.74961300	5.86803200
C	13.41549700	7.47610300	4.66953300
C	13.88588500	8.79665500	4.63940300
C	14.40063600	9.37596200	5.80792100
C	14.43071500	8.63332900	6.99866600
F	13.04045200	5.46771400	5.83715100
F	12.93692700	6.90933100	3.53850000
F	13.84568100	9.50509000	3.49002700
F	14.84304800	10.65280800	5.78140000
F	14.90747900	9.24439400	8.10006700
C	13.66027000	0.94898300	15.47347400
C	13.45323200	0.20541800	16.64425400
C	12.80534400	0.80093700	17.73593700
C	12.37681400	2.13278200	17.64566500
C	12.60791300	2.86106600	16.46802300
F	14.25146100	0.31795200	14.43397500
F	13.84928000	-1.08535900	16.72268600
F	12.59394000	0.09429000	18.86755600

F	11.76311300	2.70947700	18.70292300
F	12.20203500	4.14508300	16.44184700
H	10.47365800	2.81637600	14.42330700
H	9.18748700	3.99670800	12.35374700
H	9.44320700	5.80794500	9.44060400
H	11.06866500	6.98470400	7.62225600
H	16.04297600	2.49650000	15.39295200
H	18.15192300	3.34062900	13.93259700
H	16.72681900	7.02368700	7.45013800
H	18.56296300	5.96931900	9.12578000
O	14.09894300	6.35015600	12.18640500
O	13.01769300	6.98974900	12.46077100