Supporting Information For

Corrin ring-based structural frustration tunes the redox character of a B₁₂ cofactor: Implications for PCET-inspired catalysis

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Contents

Computational Details

References

Figure S1. Close-ups of the BP86-optimized MeCbl complexes.

Figure S2. Close-ups of the BP86-optimized AdoCbl complexes.

Figure S3. 3D redox surface of simplified MeCbl computed along $Co-N_{xx}$ coordinates.

Figure S4. Reduction potentials of MeCbl model complexes computed as a function of $Co-N_{ax}$ bond distance.

Figure S5. SOMOs of the reduced MeCbl complexes.

Figure S6. 3D redox surfaces of base-off simplified and base-off/Im-off MeCbl complexes computed along Co-N_{xx} coordinates.

Figure S7. Reduction potentials of MeCbl model complexes computed as a function of C-Co-

 N_{xx} bond angles.

Figure S8. Reduction potentials of MeCbl complexes computed as a function of C-Co-N_{ax} bond angle.

Figure S9. 3D redox surface of simplified AdoCbl computed along Co- N_{xx} coordinates.

Figure S10. Reduction potentials of AdoCbl model complexes computed as a function of $Co-N_{ax}$ bond distance.

Figure S11. SOMOs of the reduced AdoCbl complexes.

Figure S12. 3D redox surfaces of base-off simplified and base-off/Im-off AdoCbl complexes computed along Co-N_{xx} coordinates.

Figure S13. Reduction potentials of AdoCbl complexes computed as a function of C-Co- N_{xx} bond angles.

Figure S14. Reduction potentials of AdoCbl complexes computed as a function of C-Co- N_{ax} bond angle.

Table S1. Key structural features of the optimized MeCbl complexes.

Table S2. Key structural features of the optimized AdoCbl complexes.

Table S3: Experimentally determined reduction potentials of MeCbl and AdoCbl cofactors.

Table S4. Reduction potentials of simplified and full MeCbl complexes computed using avariety of DFT functionals, four different solvents and 6-31G* basis set.

Table S5. Reduction potentials of simplified and full MeCbl complexes computed using avariety of DFT functionals, four different solvents and 6-31+G basis set.

Table S6. Reduction potentials of simplified and full MeCbl complexes computed using avariety of DFT functionals, four different solvents and 6-31+G* basis set.

Table S7. Reduction potentials of simplified and full AdoCbl complexes computed using avariety of DFT functionals, four different solvents and 6-31G* basis set.

Table S8. Reduction potentials of simplified and full AdoCbl complexes computed using avariety of DFT functionals, four different solvents and 6-31+G basis set.

Table S9. Reduction potentials of simplified and full AdoCbl complexes computed using avariety of DFT functionals, four different solvents and 6-31+G* basis set.

Computational Details

To address the redox behavior of cobalt corrinoids, two biologically important B₁₂ cofactors namely MeCbl and AdoCbl cofactors were selected wherein three different types of model complexes were investigated: (1) simplified structural models with the amide side chains replaced by H's and the axial base replicated by dimethylbenzimidazole and (2) base-off/Im-on models where the nucleotide loop was terminated at the phosphodiester end and the axial base was modeled by the imidazole moiety and (3) full cofactors (Figs. S1-S2). The employed structural models of MeCbl and AdoCbl were extracted from the high resolution crystal structures of MetH (1BMT@3.0 Å res.)¹ and MCM (4REO@2.2 Å res.)² enzymes respectively that were further augmented by performing full geometry optimizations. Two different kinds of structural parameters were varied to study the redox tuning of B_{12} cofactors: (1) Co-N_{xx} (xx = 21, 22, 23, 24) and Co-N_{ax} bond lengths; (2) C-Co-N_{xx} and C-Co-N_{ax} bond angles. The choice of these parameters is driven by the fact that any perturbation in these coordinates is expected to directly impact the metal coordination site and hence the electrochemical behavior of B₁₂ cofactors. The variation in these parameters was induced to mimick the enzymatic situation. Since $\text{Co-N}_{21} \sim \text{Co-N}_{24}$ and $\text{Co-N}_{22} \sim \text{Co-N}_{23}$ in the equilibrium structures (Tables S1-S2), these bond distances were also kept fixed during the redox computations. The Co-N₂₁ ~ Co-N₂₄ bond distance was varied from 1.84 Å to 1.91 Å and from 1.83 Å to 1.91 Å in MeCbl and AdoCbl complexes respectively. Similarly the Co- N_{22} ~ Co- N_{23} bond length was systematically perturbed from 1.90 Å to 2.02 Å and from 1.88 Å to 2.02 Å in MeCbl and AdoCbl complexes respectively. The Co-Nax bond distance was changed from 2.15 Å to 2.30 Å, while the C-Co-N_{ax} bond angle was changed from 170° to 180° in both types of model complexes respectively. The C-Co- N_{xx} bond angles were varied from 90° to 96° except the C-Co- N_{24} in AdoCbl complexes that was disturbed from 90° to 105° . Both the neutral as well as the reduced forms of all the complexes were fully optimized at BP86/6-31G(d) 5d³ level of theory. All the reported calculations were carried out using Gaussian09 software.⁴ The reduction potentials of model complexes were computed using a calibrated computational protocol (BP86/6-31+G*/DMF) as described below. In order to investigate the role of the axial base in the redox modulation, the base-off analogues of the simplified and base-off/Im-on MeCbl and AdoCbl complexes were also studied. To gain atomistic insight into the reduction process, the HOMO orbitals of the reduced analogues were also analyzed.

Calibration of Computational Protocol. To calibrate the theoretical method for computing the reduction potentials of B_{12} cofactors, two kinds of structural models were selected: (1) simplified and (2) *full* cofactor models. The Born-Haber cycle-based protocol was employed to estimate the reduction potentials of the cofactors.



The reduction potential of a model complex was computed as follows:

$$E^0$$
 (vs SCE) = IP + 1/23.06 (-T Δ S + Δ G_{solvation, Redox}) - 4.52

For the standard hydrogen electrode (SHE), the absolute potential has often been reported as $-(4.44 \pm 0.02)$ eV, as recommended by the International Union of Pure and Applied Chemistry (IUPAC) in 1986.⁵ However, recently Lewis et al.⁶⁻⁷ reported a value of -4.28 eV that is considered to be the most accurate available and hence has been employed in the present analysis. Instead of choosing SHE, we referenced our computed reduction potentials with respect to the SCE that has been frequently used during the electrochemical studies of B₁₂ cofactors.⁸⁻¹¹ The standard potential of SCE is 0.24 eV more negative than that of SHE,¹² thus to compare the computed E⁰ values with the experimental ones referenced to the SCE, 4.52 V was subtracted. Also, the entropy term (-T Δ S) was dropped while computing reduction potentials as the ZPE/entropy corrections were relatively small and could be neglected as a first approximation.

Although it is generally accepted that the BP86 functional is appropriate for studying structural, electronic and spectroscopic properties of cobalt corrinoids,¹³ six other functionals that include B3LYP^{3,14}, B3PW91^{3,15-17}, PBE1PBE ^{18,19,20}, mPW1PBE^{18,19,21}, mPW3PBE^{18,19,21} and mPW1PW91^{15-17,21} were also considered during the calibration procedure. Neutral and reduced forms of all the structural models were fully optimized at the BP86/6-31G(d) 5d level of theory which were subsequently used for analysis with other basis sets (i.e., 6-31+G, and 6-31+G*, respectively) as well as with other functionals where only single point calculations were performed. Solvation effects were taken into account by performing the self-consistent reaction field (SCRF) calculations using

polarizable continuum model (PCM) within the integral equation formalism (SCRF = IEFPCM) on the gas-phase optimized geometries of the structural models. The solvation energies were evaluated employing the dielectric constants of ε =78.4 (H₂O, water), ε =46.8 (DMSO, dimethylsulfoxide) and ε =36.7 (DMF, dimethylformamide) and ε =32.6 (MeOH, methanol), respectively. These solvents were particularly selected for calibrating the computational protocol because of their prominent use in electrochemical reduction experiments of B₁₂ cofactors.⁸⁻¹¹ The detailed analysis of the experimental and the calculated reduction potentials implied that BP86/6-31+G* level of theory in combination with DMF solvent could be used as a reasonable computational protocol for addressing B₁₂ electrochemistry (see Tables S3-S9).

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Figure S1. Close-ups of the BP86-optimized MeCbl complexes (upper: simplified; middle: base-off/Im-on and bottom: full) along with key axial bond distances where the values in parentheses correspond to the reduced optimized analogues.



Figure S2. Close-ups of the BP86-optimized AdoCbl complexes (upper: simplified; middle: base-off/Im-on and bottom: full) along with key axial bond distances where the values in parentheses correspond to the reduced optimized analogues.



Figure S3. 3D redox surface of simplified MeCbl computed along Co-N_{xx} coordinates. Note here that the data is shown relative to the reduction potential corresponding to $\text{Co-N}_{21} = \text{Co-N}_{24} = 1.84 \text{ Å}$ and $\text{Co-N}_{22} = \text{Co-N}_{23} = 1.90 \text{ Å}$ that has been set equal to zero. The similar convention has been used for other MeCbl complexes as well as for AdoCbl complexes.



Figure S4. Reduction potentials of MeCbl model complexes computed along Co-N_{ax} coordinate. Note here that the reduction potentials of all the MeCbl complexes have been shown relative to the reduction potentials of the simplified MeCbl complex and the same convention has been used in the case of AdoCbl complexes.



Figure S5. SOMOs of the reduced MeCbl complexes (isosurface value = ± 0.04 ; upper: simplified; middle: base-off/Im-on and bottom: full).



Figure S6. 3D redox surfaces of base-off simplified (upper) and base-off/Im-off (lower) MeCbl complexes computed along Co-N_{xx} coordinates.



Figure S7. Reduction potentials of MeCbl model complexes computed as a function of C-Co- N_{xx} bond angles.



Figure S8. Reduction potentials of MeCbl complexes computed as a function of C-Co- N_{ax} bond angle.



Figure S9. 3D redox surface of simplified AdoCbl computed along Co- N_{xx} coordinates.



Figure S10. Reduction potentials of AdoCbl model complexes computed as a function of Co-N_{ax} bond distance.



Figure S11. SOMOs of the reduced AdoCbl complexes (isosurface value = ± 0.04 ; upper: simplified; middle: base-off/Im-on and bottom: full).



Figure S12. 3D redox surfaces of base-off simplified (upper) and base-off/Im-off (lower) AdoCbl complexes computed along $Co-N_{xx}$ coordinates.

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Figure S13. Reduction potentials of AdoCbl complexes computed as a function of C-Co- N_{xx} bond angles.



Figure S14. Reduction potentials of AdoCbl complexes computed as a function of C-Co- N_{ax} bond angle.

Table S1. Key structural features of the optimized MeCbl complexes (bond lengths are in Å units while bond angles are in degrees).

	MeCbl (neutral,reduced)								
Parameter		Calculated	Experimental						
	simplified	base-off/Im-on	full	Isolated ^a	MetH-bound ^b				
Co-C	1.97, 1.96	1.96,1.96	1.97,1.96	1.98	1.96				
Co-N _{ax}	2.18,2.16	2.15,2.11	2.15,2.16	2.16	2.24				
Co-N ₂₁	1.87,1.88	1.87,1.88	1.87,1.89	1.88	1.91				
Co-N ₂₂	1.93,1.94	1.94,1.96	1.93,1.94	1.97	2.02				
Co-N ₂₃	1.93,1.94	1.93,1.94	1.93,1.94	1.97	2.02				
Co-N ₂₄	1.87,1.88	1.87,1.89	1.87,1.88	1.87	1.91				
C-Co-N ₂₁	92.7,92.7	93.4,92.7	92.5,92.3	86.3	82.1				
C-Co-N ₂₂	86.7,86.9	89.3,88.8	86.7,87.1	94.8	90.8				
C-Co-N ₂₃	89.9,90.0	89.5,89.4	90.1,90.1	94.8	90.8				
C-Co-N ₂₄	89.4,89.9	87.9,89.2	88.5,89.6	86.3	82.1				
C-Co-N _{ax}	177.4,177.6	174.8,175.8	174.3,175.7	174.6	167.4				

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Table S2. Key structural features of the optimized AdoCbl complexes (bond lengths are in Å units while bond angles are in degrees).

	AdoCbl (neutral,reduced)								
Parameter		Calculated		Exper	imental				
	simplified	base-off/Im-on	full	Isolated ^c	GLM-bound ^d				
Co-C	1.99,1.98	2.00, 1.98	2.00, 1.99	2.03	1.96				
Co-N _{ax}	2.21,2.18	2.13,2.12	2.16,2.16	2.24	2.24				
Co-N ₂₁	1.87,1.88	1.87,1.89	1.88,1.89	1.87	1.88				
Co-N ₂₂	1.93,1.93	1.94,1.95	1.94,1.95	1.91	2.02				
Co-N ₂₃	1.93,1.94	1.93,1.94	1.93,1.94	1.91	1.93				
Co-N ₂₄	1.87,1.88	1.88,1.89	1.88,1.88	1.87	1.90				
C-Co-N ₂₁	90.8,90.4	92.1,91.8	92.2,91.9	84.0	82.1				
C-Co-N ₂₂	87.8,88.8	84.6, 84.5	83.6,83.7	93.2	90.8				
C-Co-N ₂₃	93.3,94.3	91.6, 91.8	91.5,91.6	93.2	90.8				
C-Co-N ₂₄	90.0,89.7	95.1,96.4	93.9,95.6	84.0	82.1				
C-Co-N _{ax}	179.2,179.0	170.8,170.7	170.9, 171.2	171.3	167.4				

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Table S3: Experimentally determined reduction potentials of MeCbl and AdoCbl cofactors.

Cofactor	Solvent	Redox Potential [V] vs SCE
MeCbl	DMF-Propanol	-1.60 ^{e,f}
MeCbl	DMSO	-1.60 ^f
MeCbl	DMF-Methanol	-1.47 ^{g,h}
AdoCbl	DMF-Methanol	-1.31 ^g

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Table S4. Reduction potentials of simplified and full MeCbl complexes computed using avariety of DFT functionals, four different solvents and 6-31G* basis set.

	Reduction Potential [V units] vs SCE							
Functional	simplified MeCbl			full MeCbl				
	DMF	DMSO	MeOH	H ₂ O	DMF	DMSO	MeOH	H₂O
BP86	-2.01	-2.00	-1.99	-1.98	-2.12	-2.14	-2.16	-2.15
B3LYP	-1.87	-1.86	-1.85	-1.86	-2.00	-2.01	-2.02	-2.03
B3PW91	-2.01	-2.00	-1.98	-1.99	-1.97	-1.97	-1.99	-1.99
PBE1PBE	-2.01	-2.00	-1.98	-1.98	-2.14	-2.15	-2.17	-2.18
mPW1PBE	-2.07	-2.06	-2.04	-2.04	-1.99	-1.99	-2.01	-2.03
mPW 3PBE	-1.93	-1.92	-1.90	-1.98	-1.98	-2.08	-2.00	-2.01
mPW1PW91	-2.02	-2.02	-2.00	-1.99	-2.01	-2.02	-2.03	-2.05

Table S5. Reduction potentials of simplified and full MeCbl complexes computed using avariety of DFT functionals, four different solvents and 6-31+G basis set.

	Reduction Potential [V units] vs SCE								
Functional		simpli	fied MeCbl		full MeCbl				
	DMF DMSO MeOH H ₂ O			H₂O	DMF	DMSO	MeOH	H₂O	
BP86	-1.81	-1.80	-1.79	-1.79	-1.76	-1.88	-1.92	-1.81	
B3LYP	-1.86	-1.86	-1.85	-1.86	-1.85	-1.98	-2.02	-1.91	
B3PW91	-1.84	-1.83	-1.81	-1.82	-1.84	-1.96	-2.01	-1.89	
PBE1PBE	-1.84	-1.83	-1.82	-1.82	-1.86	-1.98	-2.03	-1.91	
mPW1PBE	-1.84	-1.83	-1.82	-1.82	-1.86	-1.98	-1.71	-2.29	
mPW 3PBE	-1.82	-1.81	-1.79	-1.80	-1.83	-1.95	-1.99	-1.88	
mPW1PW91	-1.83	-1.82	-1.80	-1.81	-1.84	-1.97	-2.01	-1.89	

Table S6. Reduction potentials of simplified and full MeCbl complexes computed using avariety of DFT functionals, four different solvents and 6-31+G* basis set.

	Reduction Potential [V units] vs SCE							
Functional		simpl	ifed MeCbl		full MeCbl			
	DMF	DMF DMSO MeOH H ₂ O			DMF	DMSO	MeOH	H₂O
BP86	-1.76	-1.76	-1.74	-1.75	-1.63	-1.77	-1.81	-1.71
B3LYP	-1.84	-1.83	-1.82	-1.84	-1.77	-1.87	-1.92	-1.81
B3PW91	-1.80	-1.79	-1.78	-1.79	-1.74	-1.85	-1.89	-1.79
PBE1PBE	-1.81	-1.80	-1.78	-1.79	-1.75	-1.87	-1.91	-1.80
mPW1PBE	-1.81	-1.80	-1.78	-1.79	-1.75	-1.87	-1.91	-1.80
mPW 3PBE	-1.78	-1.77	-1.76	-1.77	-1.72	-1.83	-1.87	-1.77
mPW1PW91	-1.79	-1.79	-1.77	-1.78	-1.74	-1.85	-1.90	-1.79

Table S7. Reduction potentials of simplified and full AdoCbl complexes computed using avariety of DFT functionals, four different solvents and 6-31G* basis set.

	Reduction Potential [V units] vs SCE								
Functional		simplif	ied AdoCbl		full AdoCbl				
	DMF DMSO MeOH H ₂ O				DMF	DMSO	MeOH	H₂O	
BP86	-1.71	-1.86	-1.75	-1.76	-1.81	-1.92	-1.94	-2.04	
B3LYP	-1.84	-1.87	-1.87	-1.88	-1.93	-1.91	-2.07	-1.91	
B3PW91	-1.72	-1.75	-1.75	-1.75	-1.75	-1.85	-1.89	-2.00	
PBE1PBE	-1.81	-1.84	-1.84	-1.85	-1.56	-1.66	-1.70	-1.79	
mPW1PBE	-1.75	-1.78	-1.78	-1.78	-1.69	-1.79	-1.83	-1.92	
mPW 3PBE	-1.64	-1.66	-1.67	-1.67	-1.69	-1.79	-1.83	-1.94	
mPW1PW91	-1.78	-1.80	-1.81	-1.81	-1.79	-1.90	-1.93	-2.02	

Table S8. Reduction potentials of simplified and full AdoCbl complexes computed using avariety of DFT functionals, four different solvents and 6-31+G basis set.

	Reduction Potential [V units] vs SCE							
Functional	simplified AdoCbl DMF DMSO MeOH H ₂ O				full AdoCbl			
					DMF	DMSO	MeOH	H ₂ O
BP86	-1.57	-1.60	-1.60	-1.61	-1.55	-1.40	-1.72	-1.83
B3LYP	-1.65	-1.68	-1.69	-1.71	-1.60	-1.73	-1.78	-1.90
B3PW91	-1.61	-1.64	-1.64	-1.66	-1.60	-1.72	-1.78	-1.89
PBE1PBE	-1.60	-1.63	-1.63	-1.64	-1.59	-1.72	-1.77	-1.89
mPW1PBE	-1.61	-1.63	-1.64	-1.65	-1.60	-1.73	-1.78	-1.90
mPW 3PBE	-1.58	-1.61	-1.61	-1.63	-1.57	-1.70	-1.75	-1.87
mPW1PW91	-1.60	-1.62	-1.51	-1.64	-1.59	-1.71	-1.77	-1.88

Table S9. Reduction potentials of simplified and full AdoCbl complexes computed using avariety of DFT functionals, four different solvents and 6-31+G* basis set.

	Reduction Potential [V units] vs SCE								
Functional		simplif	ied AdoCbl		full AdoCbl				
	DMF	DMF DMSO MeOH H ₂ O				DMSO	MeOH	H₂O	
BP86	-1.56	-1.59	-1.60	-1.60	-1.45	-1.56	-1.61	-1.70	
B3LYP	-1.67	-1.70	-1.71	-1.72	-1.51	-1.62	-1.67	-1.79	
B3PW91	-1.62	-1.64	-1.65	-1.66	-1.50	-1.61	-1.66	-1.60	
PBE1PBE	-1.61	-1.63	-1.58	-1.65	-1.49	-1.60	-1.65	-1.76	
mPW1PBE	-1.62	-1.64	-1.65	-1.66	-1.50	-1.62	-1.67	-1.78	
mPW 3PBE	-1.59	-1.61	-1.62	-1.63	-1.47	-1.59	-1.63	-1.74	
mPW1PW91	-1.61	-1.63	-1.64	-1.65	-1.63	-1.22	-1.65	-1.76	