Supporting Information

for

Spectroscopic and Computational Characterization of the Base-off Forms of Cob(II)alamin

Matthew D. Liptak, Angela S. Fleischhacker, Rowena G. Matthews, Joshua Telser, and Thomas C. Brunold

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Table S1. Parameters obtained from a fit of the X-Band EPR spectrum of five-coordinate base-off Co^{2+}Cbl

	g	*A* (^{59}Co)	width	*g* -strain	*A* -strain
1	2.382	206	20	0.068	0.209
2	2.302	229	22	0.300	-0.185
3	1.992	392	19	-0.102	-0.025

Table S2. Parameters obtained from a fit of the Q-Band EPR spectrum of five-coordinate base-off Co^{2+}Cbl

	g	*A* (^{59}Co)	width	*g* -strain	*A* -strain
1	2.382	206	55	0.062	0.210
2	2.302	229	52	0.041	0.088
3	1.992	392	57	0.291	0.097

Table S3. Parameters obtained from a fit of the X-Band EPR spectrum of four-coordinate base-off Co^{2+}Cbl

	g	*A* (^{59}Co)	width	*g* -strain	*A* -strain
1	2.814	695	24	0.168	0.187
2	2.534	556	16	0.032	0.050
3	1.935	495	20	0.048	0.022

Table S4. Parameters obtained from a fit of the Q-Band EPR spectrum of four-coordinate base-off Co^{2+}Cbl

	g	*A* (^{59}Co)	width	*g* -strain	*A* -strain
1	2.814	695	50	0.071	0.086
2	2.534	556	50	0.030	0.041
3	1.935	495	53	0.131	0.057

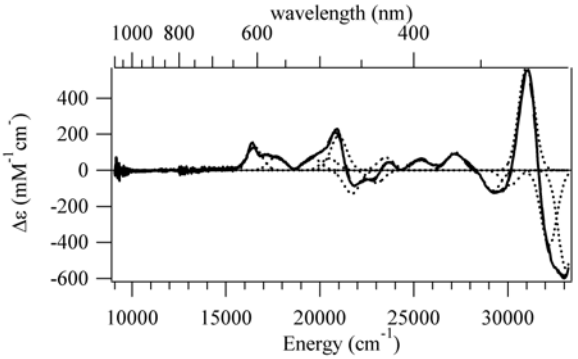

Figure S1. Gaussian deconvolution of the five-coordinate base-off Co^{2+}Cbl MCD spectrum obtained at 2K.

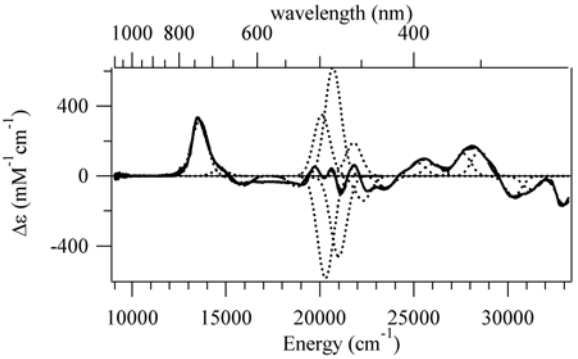

Figure S2. Gaussian deconvolution of the four-coordinate base-off Co^{2+}Cbl MCD spectrum obtained at 2K.

Table S5. Parameters obtained from the Gaussian deconvolution of the five-coordinate base-off Co^{2+}Cbl MCD spectrum (Figure S1)

Band	Energy (cm^{-1})	$\Delta\varepsilon$ ($M^{-1}cm^{-1}$)	Width (cm^{-1})
1	16500	125	1000
2	17700	75	1000
3	19600	70	1000
4	20500	65	1000
5	21000	190	1000
6	21700	-130	1000
7	23000	-70	1000
8	23500	70	1000
9	25400	65	1000
10	27200	100	1000
11	29200	-115	1000
12	30100	-85	1000
13	31000	570	1000
14	32200	-415	1000
15	33100	-545	1000

Table S6. Parameters obtained from the Gaussian deconvolution of the four-coordinate base-off Co^{2+}Cbl MCD spectrum (Figure S2)

Band	Energy (cm^{-1})	$\Delta\varepsilon$ ($M^{-1}cm^{-1}$)	Width (cm^{-1})
1	13600	315	1000
2	14700	35	1000
3	15900	-55	1000
4	18800	-60	1000
5	20100	350	1000
6	20300	-585	1000
7	20700	620	1000
8	21000	-460	1000
9	21800	190	1000
10	22300	-140	1000
11	23500	-65	1000
12	25200	75	1000
13	26000	70	1000
14	27600	130	1000
15	28500	145	1000
16	30300	-115	1000
17	31200	-75	1000
18	33000	-165	1000

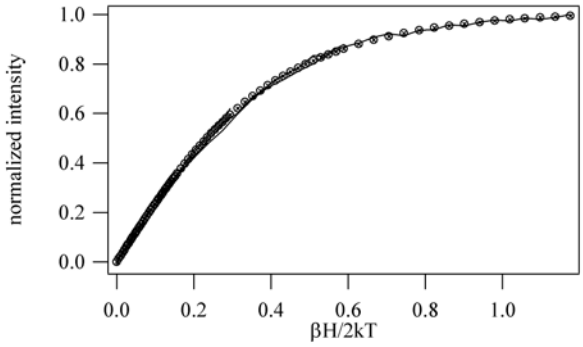

Figure S3. Experimental (solid line) and simulated (marks) VTVH MCD data at 2, 4, and 8 K for the 742 nm feature of four-coordinate, base-off Co^{2+}Cbl.

Table S7. VTVH MCD data fit parameters for the 742 feature of four-coordinate, base-off Co^{2+}Cbl

	1	2	3
g value[a]	2.81	2.53	1.94
Polarization	26.3%	11.7%	62.0%

[a] *g* values taken from the fit of the EPR spectra of four-coordinate, base-off Co^{2+}Cbl (Tables S3 and S4)

Table S8. PBE/TZP-optimized Cartesian coordinates of five-coordinate base-off Co^{2+}Cbl

Co	0.000000	0.000000	0.000000
N	-1.405273	1.230515	-0.159073
N	1.305466	1.421371	-0.018066
N	1.305191	-1.415314	-0.148926
N	-1.411148	-1.230682	-0.008240
C	-2.756851	0.685837	-0.440247
C	-3.696945	1.799240	0.037796
C	-2.845642	3.070419	-0.176315
C	-1.433014	2.539368	-0.060852
C	-0.253189	3.312012	0.094940
C	1.009613	2.773682	0.084000
C	2.279312	3.589386	0.192841
C	3.392975	2.557861	-0.035187
C	2.651474	1.242523	-0.054413
C	3.285095	0.006317	-0.127625
C	2.651031	-1.229843	-0.195129
C	3.395172	-2.536591	-0.333023
C	2.272583	-3.568268	-0.508377
C	1.008286	-2.762192	-0.307968
C	-0.253159	-3.302597	-0.315460
C	-1.435867	-2.534103	-0.164169
C	-2.851654	-3.066925	-0.133118
C	-3.696045	-1.787521	-0.321594
C	-2.772827	-0.686813	0.217743
H	-2.840286	0.546860	-1.534424
H	-3.913803	1.668503	1.108871
H	-4.648209	1.822479	-0.506805
H	-3.050903	3.867889	0.549637
H	-2.997025	3.499420	-1.180954
H	-0.350067	4.393692	0.188797
H	2.345215	4.052261	1.188492
H	2.289810	4.406662	-0.539261
H	4.167206	2.570221	0.743454
H	3.906540	2.708496	-0.996628
H	4.375290	0.008179	-0.165283
H	4.000168	-2.722855	0.566986
H	4.091644	-2.506424	-1.181641
H	2.331604	-4.397919	0.207977
H	2.276215	-4.013077	-1.513672
H	-0.349884	-4.378662	-0.459976
H	-3.042191	-3.542725	0.843384
H	-3.027191	-3.829269	-0.903168
H	-3.887451	-1.619949	-1.392334
H	-4.660950	-1.830307	0.196838
H	-2.900970	-0.553207	1.307556
O	-0.045486	0.016113	2.327423
H	0.454742	0.806503	2.607925
H	0.522110	-0.732437	2.593903

Table S9. PBE/TZP-optimized Cartesian coordinates of four-coordinate base-off Co^{2+}Cbl

Co	0.000000	0.000000	0.000000
N	-1.408340	1.228256	-0.080490
N	1.301987	1.414978	0.068817
N	1.303116	-1.414413	-0.069946
N	-1.407944	-1.228607	0.079315
C	-2.768387	0.686569	-0.330170
C	-3.695694	1.793518	0.186981
C	-2.847198	3.068069	-0.013412
C	-1.432846	2.536194	0.052231
C	-0.254303	3.305557	0.207123
C	1.006485	2.764343	0.201508
C	2.272324	3.572693	0.369598
C	3.390289	2.545685	0.149673
C	2.649078	1.234406	0.071671
C	3.284363	0.001465	-0.007751
C	2.649948	-1.232224	-0.081894
C	3.393005	-2.542053	-0.167358
C	2.274139	-3.574844	-0.353882
C	1.008270	-2.764496	-0.195602
C	-0.252411	-3.306000	-0.201447
C	-1.431549	-2.536667	-0.052444
C	-2.846024	-3.068924	0.007370
C	-3.694031	-1.794662	-0.197021
C	-2.769211	-0.687363	0.323639
H	-2.881653	0.555038	-1.422379
H	-3.895416	1.640533	1.258347
H	-4.656021	1.829834	-0.340317
H	-3.033722	3.846176	0.737885
H	-3.020157	3.523880	-1.002518
H	-0.350906	4.384079	0.330795
H	2.304886	4.003387	1.380966
H	2.306320	4.410828	-0.337692
H	4.137665	2.533432	0.953796
H	3.935440	2.718491	-0.790482
H	4.374893	0.002090	-0.011856
H	3.964020	-2.706528	0.758545
H	4.118744	-2.531998	-0.991348
H	2.313950	-4.392731	0.376740
H	2.299927	-4.034393	-1.352402
H	-0.348495	-4.385010	-0.321243
H	-3.023285	-3.524734	0.995697
H	-3.028900	-3.847061	-0.744827
H	-3.889206	-1.642075	-1.269287
H	-4.656631	-1.831039	0.326172
H	-2.886734	-0.555832	1.415405