Supporting Information

Analysis of the Cob(II)alamin – 5′-Deoxy-3′,4′-Anhydroadenosyl Radical Triplet Spin System in the Active Site of Diol Dehydrase

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The spin densities and corresponding hyperfine splitting parameters were obtained from B3LYP/TZVP//B3LYP/6-31G* calculations using *Gaussian 98*. This combination has been shown to give good agreement with experimental determinations of hyperfine parameters for nuclei in the first three rows of the periodic table (*1,2*). The calculated hyperfine parameters for the nitrogen ligands are in good agreement with the available experimental data (A_{iso} = 16 G and 20 G for the calculated and experimental axial nitrogen ligand of base-on cob(II)alamin, respectively, and A_{iso} = 0.8 G and between 0.8-1.2 G for the calculated and experimental equatorial nitrogen ligands of base-on cob(II)alamin and base-off cob(II)alamin (and related Co^{2+} complexes of macrocyclic ligands), respectively) (*3,4,5*). The calculated hyperfine parameters of the central cobalt are larger than those observed experimentally (A_{iso} = 133 G versus 44 G for the calculated and experimental Co^{2+} hyperfine parameters). However, the calculated spin density of cobalt (ρ = 1.01), which is the parameter that is used in the calculation of the ZFS tensor, is likely fairly close to the actual value. The calculated atomic spin densities of the truncated cob(II)alamin structure and the anhydroadenosyl radical, and the corresponding numbering systems, are given in Tables S1 and S2 and Figure S1,

respectively. As can be seen from the tables, spin is substantially delocalized with many atoms having significant negative spin density due to spin polarization effects (particularly in the anhydroadenosyl radical), thus necessitating the inclusion of spin density of more atoms than just the cobalt of cob(II)alamin and the 5′- and 3′-carbons of the anhydroadenosyl radical in the expression for the ZFS tensor. Atoms having less than 1% spin density can be excluded from the calculations although their inclusion does not alter the speed of the calculations appreciably.

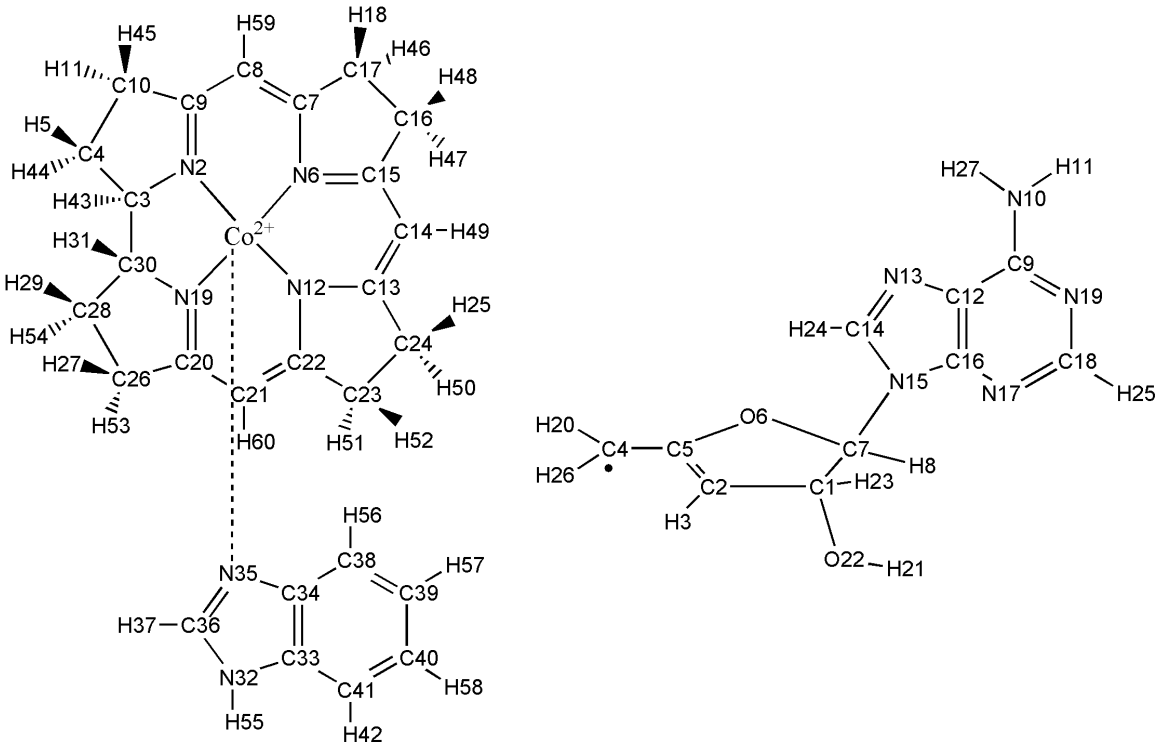

Figure S1. Numbering system used in the *Gaussian 98* single-point energy calculations on the truncated cob(II)alamin structure and the anhydroadenosyl radical.

Table S1. Calculated atomic spin densities and hyperfine parameters for truncated cob(II)alamin.					
	Atom	Spin Density	A_x	A_y	A_z
1	Co	1.010	51.8	80.0	267.5
2	N	0.027	-1.4	-1.2	0.7
3	C	-0.007	-1.0	-0.9	-0.2
4	C	0.000	-0.1	-0.0	0.2
5	H	-0.000	-0.4	-0.3	0.6
6	N	0.012	-1.3	-0.9	-0.2
7	C	-0.051	-5.6	-1.8	-1.1
8	C	0.053	1.5	2.2	5.0
9	C	-0.038	-4.7	-1.9	-1.1
10	C	0.004	0.2	0.2	0.5
11	H	-0.002	-1.7	-1.6	-0.9
12	N	0.006	-1.3	-1.1	-0.5
13	C	-0.030	-3.3	-1.0	-0.3
14	C	0.027	0.6	1.3	2.4
15	C	-0.036	-3.9	-1.4	-0.6
16	C	0.002	0.1	0.1	0.3
17	C	0.004	0.5	0.5	0.8
18	H	-0.003	-2.2	-2.2	-1.6

19	N	0.004	-1.2	-0.9	-0.7
20	C	-0.020	-1.7	-0.5	0.2
21	C	0.018	0.2	0.8	1.3
22	C	-0.018	-1.7	-0.7	0.0
23	C	0.001	-0.1	-0.1	0.1
24	C	0.002	0.1	0.1	0.3
25	H	-0.001	-1.3	-1.3	-0.7
26	C	0.000	-0.0	-0.0	0.2
27	H	-0.001	-0.9	-0.9	-0.1
28	C	-0.000	-0.2	-0.2	0.1
29	H	-0.000	-0.3	-0.2	0.4
30	C	-0.002	-0.1	0.0	0.7
31	H	0.000	-0.7	-0.7	1.7
32	N	0.001	0.6	0.6	0.8
33	C	0.006	1.2	1.2	1.7
34	C	0.003	0.9	1.1	2.3
35	N	0.045	14.7	14.9	17.9
36	C	-0.004	-0.9	-0.1	0.6
37	H	0.000	-0.5	-0.3	2.2
38	C	-0.005	-0.6	-0.3	0.0
39	C	0.001	0.0	0.1	0.2
40	C	0.000	-0.1	-0.1	0.0

41	C	-0.001	-0.3	-0.2	0.0
42	H	0.001	0.4	0.4	0.7
43	H	0.003	1.1	1.2	3.6
44	H	-0.000	-0.3	-0.2	0.5
45	H	-0.001	-1.2	-1.2	-0.5
46	H	-0.001	-1.5	-1.5	-0.9
47	H	-0.001	-1.5	-1.4	-0.8
48	H	-0.001	-1.1	-1.1	-0.6
49	H	-0.001	-1.2	-0.8	0.3
50	H	-0.001	-1.2	-1.1	-0.5
51	H	-0.001	-0.7	-0.7	-0.0
52	H	-0.000	-0.6	-0.6	0.0
53	H	-0.000	-0.4	-0.3	0.3
54	H	0.000	-0.3	-0.3	0.7
55	H	0.001	0.2	0.3	0.9
56	H	0.001	-0.3	-0.1	1.8
57	H	0.000	-0.1	-0.1	0.3
58	H	0.000	0.0	0.0	0.3
59	H	-0.004	-2.5	-1.8	-0.3
60	H	-0.001	-0.8	-0.5	0.50

Table S2. Calculated atomic spin densities and hyperfine parameters for anhydroadenosyl radical.

	Atom	Spin Density	A_x	A_y	A_z
1	C	-0.055	-8.9	-8.7	-7.6
2	C	0.698	0.9	1.4	55.7
3	H	-0.026	-23.1	-15.6	-5.8
4	C	0.681	-0.5	-0.0	48.9
5	C	-0.274	-28.9	-14.9	-12.8
6	O	-0.011	4.6	0.2	-0.4
7	C	0.006	3.0	3.1	3.9
8	H	-0.002	-1.5	-1.2	0.6
9	C	-0.000	-0.0	-0.0	0.0
10	N	-0.000	-0.0	-0.0	0.0
11	H	-0.000	-0.0	-0.0	0.1
12	C	0.000	-0.0	-0.0	0.1
13	N	0.000	-0.0	-0.0	0.0
14	C	0.000	-0.1	-0.0	0.1
15	N	-0.000	-0.1	-0.1	0.0
16	C	0.002	-0.1	-0.1	0.1
17	N	0.000	0.3	0.3	0.4
18	C	0.000	-0.0	-0.0	0.1

19	N	0.000	-0.0	-0.0	0.0
20	H	-0.034	-22.5	-14.3	-5.3
21	H	0.002	-0.3	0.1	1.6
22	O	0.008	-5.1	-5.3	-7.7
23	H	0.036	25.9	27.0	29.4
24	H	0.000	-0.2	-0.1	0.4
25	H	0.000	-0.1	-0.1	0.2
26	H	-0.032	-20	-14.0	-5.2
27	H	-0.000	-0.0	-0.0	0.1

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