Electronic Supplementary Material (ESI) for Chemical Science.

A five-coordinate Mn(IV) intermediate in biological water oxidation: spectroscopic signature and a pivot mechanism for water binding

Marius Retegan, Vera Krewald, Fikret Mamedov, Frank Neese, Wolfgang Lubitz, Nicholas Cox and Dimitrios A. Pantazis**

SUPPORTING INFORMATION

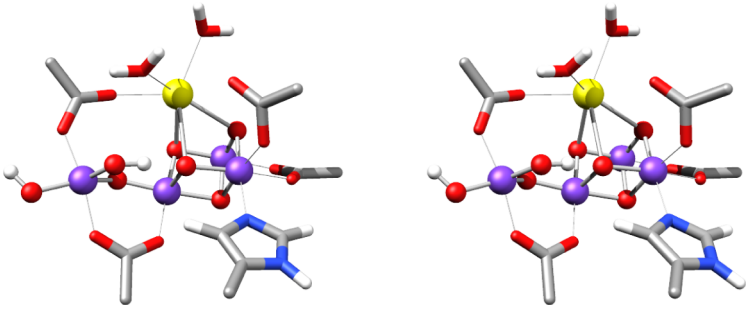

Fig. S1. Three-dimensional representation of the OEC core in the optimized S_3^B model. Selected amino acid side chains are shown for orientation.

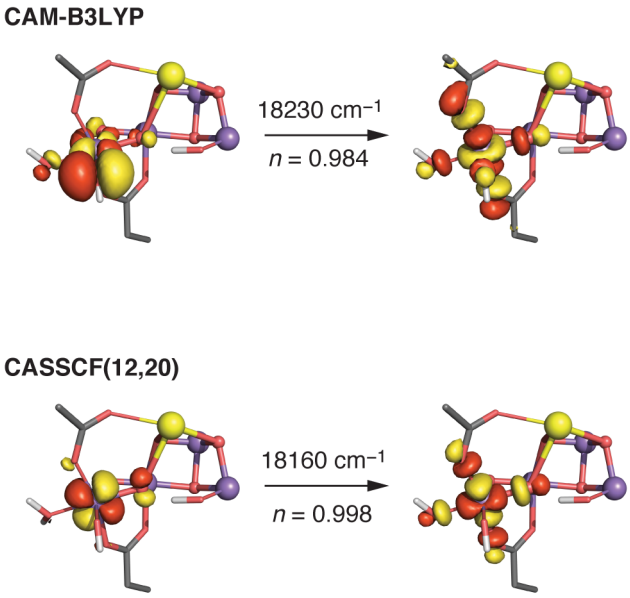

Fig. S2. Top: $S_3^{A,W}$ natural transition orbital pair for the lowest-energy transition, as obtained from CAM-B3LYP TD-DFT calculations. Bottom: CASSCF orbitals in the first excited state.

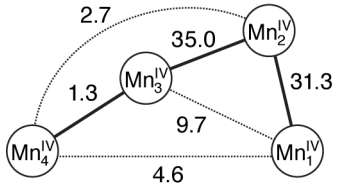

Fig. S3. Exchange coupling constants J_{ij} (cm^{-1}) for the S_3^B model.

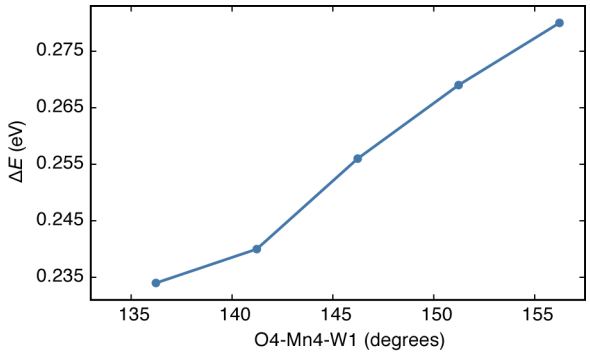

Fig. S4. Correlation between the $d_{yz}-d_{z^2}$ orbital energy difference for the Mn4 ion of S_3^B and the O4-Mn4-W1 angle.

Table S1. Relative energies (kcal mol^{-1}) of deprotonated S_2Y_Z and $S_2Y_Z^{\bullet}$ models, referenced to the lowest-energy isomer (open-cubane A-type form) for each oxidation state.

Site	$S_2^AY_Z$	$S_2^BY_Z$	$S_2^AY_Z^{\bullet}$	$S_2^BY_Z^{\bullet}$
W1a	0.0	15.7	0.0	14.2
W1b	16.3	29.4	16.6	27.4
W2	17.9	29.2	17.1	25.0
W3a	56.4	59.7	39.4	40.3
W3b	50.6	53.8	35.6	35.5
W4a	50.6	50.2	34.6	34.1
W4b	51.5	50.6	36.3	35.2

Table S2. Relative energies (kcal mol^{-1}) of products of water addition to S_3^B at different binding sites and various hydrogen-bonding configurations. H_a and H_b refer to the nomenclature of Figure 3 in the main text.

model	E_{rel} (kcal/mol)	W_{new} position and H-bonding
$S_3^{B,W}$_outside-1	0.0	"outside" at Mn4, bound at the site equivalent to W1 position in S_2 H_a forms H-bond with Asp61, H_b points towards Ser169
$S_3^{B,W}$_outside-2	3.8	"outside" at Mn4, bound at the site equivalent to W1 position in S_2 H_a forms H-bond with Asp61, H_b points towards Arg357
$S_3^{B,W}$_inside-1	10.5	"inside" at Mn4, bound at the site *trans* to the S_2 state W1 position H-bonds with W3 and O5
$S_3^{B,W}$_inside-2	10.7	"inside" at Mn4, bound at the site *trans* to the S_2 state W1 position H-bond only with O5
$S_3^{A,W}$_inside-1	12.4	"inside" at Mn1, bound at the site that is empty in the S_2 state one proton forms H-bond with Glu189 carboxylate-O, the other transferred to O5 and H-bonding with O(W_{new})

EPR signals of trapped reduced-cluster states.

The EPR signal induced by NIR illumination arises from the OEC cluster and the $Y_Z^{\bullet}$ radical. The intermediate responsible for the signal is similar, but not identical, to the transient formed during electron shuttling between the Mn cofactor and $P680^{\bullet+}$ under physiological advancement presented above; it results instead from the one-electron oxidation of tyrosine Y_Z by the OEC cofactor, an $S_2'Y_Z^{\bullet}$ state.[1, 2] Because structural relaxations are limited at the cryogenic temperatures used in experiments, S_2' designates a state of the cluster that is electronically similar to S_2, but with a geometric structure that is similar to its parent (S_3) structure. In parallel with the formation of a signal at $g \approx 2$, characteristic of the presence of the $Y_Z^{\bullet}$ radical, broadened due to the interaction with the OEC cluster, a derivative-shaped signal associated with the cluster itself is observed at $g \approx 5$. The feature was assigned to a high spin $S = 7/2$ configuration of the cluster, reminiscent of the $S = 5/2$ configuration responsible for the $g = 4.1$ signal seen in the S_2 state.[3]

The low-field part of the spectrum at $g \approx 5$ displays interesting similarities with the signal detected previously in samples that have undergone multiple turnovers above the S_1 state and were subsequently stored in liquid nitrogen for prolonged periods of time.[4] Centered at $g = 5$, the signal was assigned to the same $S = 7/2$ ground state of the manganese cluster.[3] To account for the subtle differences in the field position and line shape of the two signals, a more relaxed structure of the OEC cluster was assumed following incubation at 77K.

Attempts to computationally determine a structural candidate for the measured EPR signal generated by NIR illumination are hindered by the very mechanism of intramolecular electron transfer responsible for its formation, a problem that cannot be treated adequately within the present ground-state DFT approach. The comparable EPR signal measured in samples advanced

to the S_3 state and subsequently stored for extended periods of time at liquid nitrogen temperature, point towards a very similar structural configuration of the OEC cluster being formed even in the absence of the $Y_Z^{\bullet}$ radical. In this case the reduced S_2'' state is generated via charge recombination of the cluster with the plastoquinone Q_A^-. This state, which contains a reduced Y_Z residue, can be approximated by one-electron reduction of the S_3^B structure.

The optimized geometrical parameters indicate that the structural differences between the parent and reduced structures are minimal. As expected, the largest differences are observed in the coordination environment of the Mn center that changes oxidation state, here the five-coordinate Mn4. We have fitted a set of six coupling constants to the energies of the different broken symmetry calculations for the reduced model. Very small differences are observed for all exchange coupling constants with the exception of J_{34}, which switches from weak ferromagnetic to antiferromagnetic. In general, J_{34} is sensitive to small structural perturbations and hence we consider it as the least well-defined parameter in the present simulations. Diagonalization of the Heisenberg Hamiltonian results in a ground state that is fourteen times degenerate, but with an extremely dense spacing of excited states at the low-energy manifold of the spin ladder. Five spin states are present below 6.5 cm^{-1}, with the remaining states appearing at significantly higher energy with respect to the ground state. The $S = 7/2$ state inferred experimentally as responsible for the $g = 5$ EPR signal, is only 5 cm^{-1} above the higher-spin ground state inferred from the calculated exchange coupling constants. Therefore, the high-spin nature of such species that contain an inorganic cluster reduced with respect to the parent S_3 structure are consistent with the parent structure being assigned as the S_3^B model.

Cartesian Coordinates

S3B

Mn	-25.051656	-35.482828	203.983036
Mn	-27.385034	-35.236831	205.423907
Mn	-27.060142	-33.508890	203.297301
Mn	-27.774445	-32.837195	200.198368
Ca	-27.850756	-36.802494	202.344305
O	-26.489108	-36.544962	204.459622
O	-28.254373	-34.772967	203.904484
O	-25.975989	-34.066374	204.833338
O	-28.189776	-33.085634	201.949846
O	-25.977044	-34.850660	202.476034
O	-28.102726	-31.895575	198.706546
O	-26.414112	-34.013685	199.993347
O	-27.575670	-37.326782	200.026893
O	-28.262579	-39.195669	202.585433
H	-30.520106	-26.882433	200.170264
C	-30.251370	-27.118690	201.216610
H	-30.741380	-26.370660	201.865470
C	-28.724639	-27.140773	201.394614
C	-28.022414	-28.199020	200.517427
O	-28.629400	-29.306235	200.325363
O	-26.873890	-27.916906	200.036841
C	-32.915980	-41.871290	196.503730
C	-31.522784	-41.499776	195.963010
C	-30.540419	-41.325391	197.109726
C	-29.961998	-42.451565	197.735913
C	-30.245984	-40.052140	197.646408
C	-29.119881	-42.324483	198.853100
C	-29.403097	-39.904781	198.761262
C	-28.837104	-41.041653	199.370914
O	-27.984686	-40.862168	200.446233
H	-33.788290	-32.330730	197.916680
C	-32.849000	-31.803550	197.687630
C	-31.628903	-32.697334	197.576972
O	-30.508457	-32.236623	197.278754
H	-32.659116	-31.043868	198.466209
N	-31.845655	-34.032739	197.779544
C	-30.825100	-35.059340	197.615270
C	-31.067523	-35.978376	196.395723
O	-30.476825	-37.065305	196.293465
C	-30.557084	-35.843374	198.911480
C	-29.746850	-35.104225	199.978472
O	-29.642472	-35.589565	201.137391
O	-29.169710	-34.022085	199.562907
N	-31.878983	-35.460688	195.437719
C	-31.934650	-35.982310	194.075970
H	-31.196480	-35.450990	193.449910
H	-21.517040	-41.190080	202.040930
C	-22.362150	-41.461160	202.714540
C	-22.802091	-42.905624	202.588368
O	-23.581647	-43.421586	203.410131
C	-23.569904	-40.509526	202.481263
C	-23.185797	-39.034669	202.680764
C	-24.330011	-38.020527	202.694839
O	-25.442954	-38.211112	202.152516
O	-24.006190	-36.912781	203.311309
N	-22.295440	-43.587288	201.522333
C	-22.675520	-44.953280	201.229430
H	-21.778710	-45.520280	200.899670
C	-23.788506	-45.071323	200.162068
C	-25.044057	-44.398184	200.603377
C	-25.570512	-43.152495	200.309786
N	-25.884878	-44.918453	201.577583
C	-26.862850	-44.014617	201.845200
N	-26.695577	-42.933776	201.085122
H	-19.267770	-31.506790	202.779430
C	-20.117520	-31.320810	202.088720
C	-21.111951	-30.478354	202.870203
O	-21.312802	-30.675766	204.091891
C	-20.819270	-32.615451	201.578612
C	-21.721191	-33.301231	202.562857
C	-23.059584	-33.657724	202.493310
N	-21.292577	-33.762586	203.802220
C	-22.317438	-34.368838	204.439124
N	-23.408681	-34.323401	203.662027
N	-21.811928	-29.565687	202.157840
C	-22.904240	-28.809840	202.755200
H	-22.570650	-28.449390	203.750770
C	-24.174662	-29.670558	202.967461
C	-24.836108	-30.135105	201.669614
C	-25.833173	-31.268075	201.785254
O	-25.836204	-32.015251	202.833842
O	-26.574774	-31.426840	200.753908
H	-25.025981	-28.877744	209.179328
C	-25.296480	-29.695510	209.871270
H	-25.221470	-29.303890	210.899300
C	-24.358708	-30.908853	209.689655
C	-24.302033	-31.412057	208.279054
C	-25.104843	-32.295489	207.579119
N	-23.352917	-30.981943	207.355080
C	-23.547060	-31.570163	206.156931
N	-24.616112	-32.366664	206.286053
H	-24.695610	-37.360580	210.154300
C	-25.331130	-37.102090	209.277670
C	-26.310252	-38.206937	208.882370
O	-26.059966	-39.035493	207.984960
C	-24.383902	-36.722422	208.122859
C	-25.042856	-36.084052	206.904534
O	-26.268126	-35.720120	207.014452
O	-24.314709	-35.947963	205.855560
N	-27.496534	-38.221198	209.557851
C	-28.416010	-39.351920	209.476350
C	-29.294010	-39.462962	208.222336
O	-29.788636	-40.555810	207.900264
N	-29.521825	-38.302562	207.565103
C	-30.187655	-38.240798	206.268650
C	-29.450809	-37.238812	205.375540
O	-29.603198	-37.246647	204.144854
O	-28.717903	-36.390699	206.061146
O	-25.145632	-37.693649	197.689889
O	-27.125484	-35.773006	197.961163
O	-26.160402	-29.908518	198.294016
O	-24.344190	-31.957926	198.910999
O	-29.450366	-30.485336	202.460518
O	-25.786456	-39.435209	199.773165
O	-27.093441	-39.097883	205.246846
H	-30.307125	-30.647063	208.993297
C	-31.002900	-31.050390	208.234240
H	-31.846730	-31.523750	208.766240
C	-30.302920	-32.075189	207.330614
C	-29.095584	-31.494169	206.566351
C	-28.349237	-32.544485	205.767008
O	-28.157861	-33.677746	206.345321
O	-27.943493	-32.231769	204.590732
H	-36.667120	-31.815043	206.878892
C	-36.975090	-32.284910	205.926020
C	-35.746508	-32.726206	205.095106
C	-34.758735	-33.621785	205.868833
C	-33.696763	-34.341490	205.022188
N	-32.681486	-33.438335	204.447923
C	-31.698512	-33.847921	203.613423
N	-31.575930	-35.154365	203.312000
N	-30.857025	-32.978798	203.037814
O	-27.486336	-29.373776	204.066221
H	-32.851584	-42.788918	197.119050
H	-33.291807	-41.069357	197.167271
H	-33.691740	-42.053250	195.737530
H	-31.579815	-40.565774	195.372419
H	-31.163761	-42.290848	195.276012
H	-30.174429	-43.455963	197.343139

H	-28.678056	-43.213866	199.317427
H	-29.154577	-38.913396	199.161927
H	-30.659850	-39.149421	197.177514
H	-27.518268	-41.797881	200.778531
H	-25.215235	-42.407069	199.595527
H	-27.663497	-44.177997	202.568251
H	-28.982513	-37.476565	207.835769
H	-27.640626	-37.537408	210.299448
H	-21.620947	-29.461817	201.163041
H	-21.698281	-43.092146	200.862677
H	-23.016802	-45.406032	202.176832
H	-23.966308	-46.144006	199.955571
H	-23.451229	-44.611973	199.215764
H	-22.488393	-38.700471	201.885423
H	-23.973590	-40.667909	201.463583
H	-21.996317	-41.326613	203.750492
H	-22.635135	-38.901445	203.630168
H	-24.377765	-40.784790	203.184120
H	-26.346747	-29.974157	209.675386
H	-25.970926	-32.882106	207.887936
H	-22.919316	-31.410520	205.270411
H	-23.782529	-33.501368	201.692865
H	-22.254845	-34.846837	205.415958
H	-19.710351	-30.778196	201.217368
H	-23.111815	-27.935750	202.115621
H	-29.892390	-34.519088	197.358478
H	-32.779352	-34.330817	198.062050
H	-32.965436	-31.263928	196.731334
H	-32.245714	-34.523531	195.598290
H	-30.685327	-28.106687	201.449483
H	-20.048445	-33.325990	201.223630
H	-21.439624	-32.363333	200.699897
H	-25.908190	-36.212140	209.591630
H	-30.086476	-39.229271	205.784754
C	-31.678626	-37.868496	206.377944
H	-32.145353	-37.863505	205.377097
H	-32.202570	-38.615775	206.997047
H	-31.800294	-36.876115	206.848309
H	-29.091856	-39.304672	210.347804
H	-27.846440	-40.296220	209.551350
H	-23.613141	-36.014032	208.481742
H	-23.838112	-37.610833	207.757739
H	-29.950953	-36.734203	198.653656
H	-31.488213	-36.222675	199.370316
H	-31.398227	-30.196402	207.653728
H	-29.958586	-32.934809	207.933844
H	-28.363907	-31.070851	207.285658
H	-31.021873	-32.490115	206.595919
H	-29.376614	-30.673667	205.883172
H	-28.277260	-26.153187	201.180442
H	-28.461858	-27.383788	202.444485
H	-24.687533	-31.739831	210.339243
H	-23.333638	-30.647745	210.012151
H	-25.064051	-32.997701	205.560006
H	-37.552410	-31.538150	205.353920
H	-35.218514	-31.827190	204.718502
H	-35.324314	-34.422399	206.383610
H	-33.184180	-35.085874	205.664414
H	-37.631483	-33.141729	206.162816
H	-36.094324	-33.271421	204.194711
H	-34.261764	-33.042443	206.673546
H	-32.742926	-32.442551	204.650222
H	-34.189347	-34.894373	204.197608
H	-30.941408	-31.961771	203.108811
H	-31.969413	-35.876583	203.906526
H	-29.978981	-33.310409	202.606305
H	-30.826404	-35.443373	202.672551
H	-23.892429	-30.552203	203.567614
H	-25.355059	-29.312088	201.141073
H	-24.908221	-29.097572	203.564260
H	-24.092520	-30.536963	200.946649
H	-20.365880	-33.615068	204.199919
H	-26.109986	-34.416117	200.869144
H	-28.895535	-32.172580	198.164969
H	-29.247937	-29.993563	201.574937
H	-28.893373	-31.292982	202.381992
H	-27.147977	-30.246706	204.343995
H	-28.252577	-29.655209	203.488644
H	-32.944125	-35.838898	193.658047
H	-31.690883	-37.056052	194.091020
H	-26.573726	-40.033182	199.930734
H	-25.542984	-39.130177	200.693108
H	-27.921834	-39.586929	203.421370
H	-27.527475	-36.719000	199.213400
H	-26.338690	-36.347140	197.743892
H	-26.768164	-35.051056	198.538723
H	-25.193539	-38.158277	196.833129
H	-25.341841	-38.397209	198.364831
H	-28.183362	-39.872290	201.859718
H	-26.936144	-38.055449	199.813628
H	-24.963643	-32.647592	199.230490
H	-24.951631	-31.180916	198.726726
H	-26.935219	-30.511682	198.425479
H	-26.364869	-29.192712	198.976543
H	-26.889313	-39.227607	206.200895
H	-26.706973	-38.206928	205.046077
H	-25.767041	-45.813502	202.049984
H	-22.597365	-30.324384	207.551999

TS model for water binding

Mn	-25.018257	-35.493159	204.009609
Mn	-27.376119	-35.247249	205.414554
Mn	-27.035899	-33.537749	203.261686
Mn	-27.543405	-32.965055	200.126004
Ca	-27.762231	-36.873173	202.335097
O	-26.445829	-36.560543	204.481760
O	-28.214020	-34.802987	203.876295
O	-25.964158	-34.073990	204.826418
O	-28.051687	-33.155718	201.837839
O	-25.920963	-34.897530	202.487293
O	-27.549839	-32.116504	198.465625
O	-26.235376	-34.182284	199.985977
O	-27.404149	-37.476699	200.027074
O	-28.150216	-39.265219	202.636088
C	-32.915382	-41.867907	196.503232
C	-31.686972	-41.037900	196.080090
C	-30.661732	-40.951518	197.199418
C	-29.867574	-42.075315	197.521040
C	-30.502329	-39.793586	197.992813
C	-28.957151	-42.056214	198.588970
C	-29.594164	-39.752155	199.066251
C	-28.821833	-40.889961	199.374059
O	-27.919748	-40.828409	200.419369
H	-31.749553	-34.524043	197.899322
C	-30.824951	-35.055921	197.615397
H	-31.031953	-35.694479	196.734973
C	-30.275100	-35.898264	198.770632
C	-29.484596	-35.158314	199.841205
O	-29.323779	-35.652208	200.973166
O	-28.941993	-34.037615	199.423124
H	-21.615410	-41.195356	201.941962
C	-22.362233	-41.457632	202.715189
C	-22.803503	-42.901324	202.588257
O	-23.558074	-43.430227	203.425733
C	-23.582110	-40.508257	202.618635
C	-23.149976	-39.033281	202.635857
C	-24.281972	-38.013785	202.716687
O	-25.396855	-38.185260	202.168838
O	-23.954870	-36.936690	203.377118
N	-22.322924	-43.572251	201.503953
C	-22.675275	-44.949679	201.229839
H	-21.775854	-45.485650	200.875916
C	-23.803043	-45.107656	200.182868
C	-25.064148	-44.433289	200.605461
C	-25.611151	-43.213321	200.249446
N	-25.902583	-44.921912	201.597947

C	-26.900530	-44.025760	201.814386
N	-26.748037	-42.980511	201.003283
H	-19.304547	-31.605586	202.778049
C	-20.118029	-31.317136	202.090207
C	-21.140983	-30.516393	202.885247
O	-21.395370	-30.768300	204.083779
C	-20.831029	-32.587982	201.518374
C	-21.704655	-33.318134	202.501391
C	-23.039969	-33.692220	202.458277
N	-21.250831	-33.769913	203.735927
C	-22.262631	-34.373517	204.397680
N	-23.366993	-34.343145	203.641106
N	-21.790395	-29.553618	202.189251
C	-22.904942	-28.806341	202.756540
H	-22.590077	-28.384738	203.728961
C	-24.158508	-29.675086	202.954786
C	-24.613061	-30.293890	201.638142
C	-25.665713	-31.374858	201.728571
O	-25.756355	-32.068569	202.796271
O	-26.339745	-31.528272	200.646376
H	-24.950067	-28.888474	209.199228
C	-25.297896	-29.692548	209.872303
H	-25.238898	-29.316732	210.908430
C	-24.423734	-30.957561	209.730405
C	-24.345805	-31.472990	208.327052
C	-25.148708	-32.350871	207.620951
N	-23.377791	-31.059193	207.415521
C	-23.564168	-31.653603	206.218034
N	-24.642857	-32.436418	206.337014
H	-24.732989	-37.477093	210.129019
C	-25.332123	-37.099094	209.278261
C	-26.293403	-38.219160	208.880524
O	-25.999685	-39.086055	208.034048
C	-24.373546	-36.700137	208.145340
C	-25.026584	-36.056983	206.926712
O	-26.255836	-35.708461	207.024810
O	-24.285976	-35.909785	205.886336
N	-27.500650	-38.215074	209.519373
C	-28.416915	-39.349086	209.476480
C	-29.313960	-39.503755	208.240702
O	-29.860774	-40.591888	207.993533
N	-29.459507	-38.388270	207.494940
C	-30.070521	-38.383575	206.170038
C	-29.401157	-37.293335	205.326068
O	-29.543889	-37.272074	204.097194
O	-28.697234	-36.432141	206.036508
O	-24.784249	-37.851907	197.850863
O	-26.801062	-35.951331	197.946495
O	-25.583364	-39.583880	199.862779
O	-26.922811	-39.141317	205.246450
H	-30.324525	-30.487784	208.904524
C	-31.004076	-31.047608	208.234585
H	-31.776701	-31.528535	208.860328
C	-30.239387	-32.105202	207.418057
C	-29.135359	-31.512626	206.516672
C	-28.369982	-32.556068	205.714192
O	-28.156855	-33.682850	206.307943
O	-27.972888	-32.245446	204.536488
H	-32.598812	-42.866724	196.858474
H	-33.441284	-41.378260	197.344128
H	-33.652078	-42.032949	195.695389
H	-32.002217	-40.020786	195.779377
H	-31.219765	-41.499455	195.187815
H	-29.961369	-42.990827	196.920272
H	-28.345794	-42.939041	198.811392
H	-29.451852	-38.840027	199.658543
H	-31.100710	-38.899625	197.767773
H	-27.514641	-41.811742	200.703047
H	-25.259868	-42.493167	199.507905
H	-27.701713	-44.167874	202.541268
H	-28.891269	-37.569417	207.726734
H	-27.677480	-37.486676	210.209408
H	-21.531378	-29.390959	201.218245
H	-21.742637	-43.071937	200.833530
H	-22.982828	-45.405692	202.186893
H	-23.971609	-46.187893	200.010289
H	-23.479419	-44.675071	199.219214
H	-22.580440	-38.789843	201.715129
H	-24.143125	-40.730341	201.691995
H	-21.872324	-41.339145	203.700087
H	-22.464908	-38.835008	203.479040
H	-24.269746	-40.712894	203.459573
H	-26.353471	-29.909263	209.632637
H	-26.028254	-32.922829	207.919249
H	-22.926420	-31.509663	205.336964
H	-23.779300	-33.567794	201.667637
H	-22.181236	-34.837761	205.380091
H	-19.676483	-30.741550	201.259135
H	-23.116745	-27.962068	202.078636
H	-30.083055	-34.303902	197.298080
H	-20.063668	-33.275314	201.113638
H	-21.470900	-32.297720	200.666221
H	-25.894789	-36.223119	209.646328
H	-29.815299	-39.337295	205.669046
C	-31.601028	-38.224458	206.206855
H	-32.007973	-38.234837	205.181382
H	-32.037443	-39.064693	206.772111
H	-31.884374	-37.276551	206.697066
H	-29.073121	-39.293865	210.362184
H	-27.844428	-40.291679	209.549854
H	-23.610703	-35.992445	208.521714
H	-23.819649	-37.582300	207.777006
H	-29.533691	-36.629909	198.387256
H	-31.056021	-36.492134	199.277596
H	-31.506561	-30.314321	207.576822
H	-29.782155	-32.847592	208.097693
H	-28.379465	-30.982636	207.133847
H	-30.947733	-32.669357	206.781254
H	-29.538581	-30.766765	205.809023
H	-24.823267	-31.763948	210.371077
H	-23.398520	-30.751568	210.090819
H	-25.096323	-33.063643	205.600919
H	-23.938816	-30.476027	203.678895
H	-24.963429	-29.532824	200.918528
H	-24.962928	-29.055083	203.391057
H	-23.755129	-30.799841	201.145567
H	-20.322358	-33.605914	204.122237
H	-26.006889	-34.560918	200.899138
H	-28.085509	-32.634633	197.828552
H	-26.417236	-40.125811	199.972182
H	-25.431982	-39.203299	200.776408
H	-27.772702	-39.642400	203.462926
H	-27.314906	-36.878860	199.217187
H	-25.987994	-36.516971	197.825370
H	-26.512436	-35.217661	198.550093
H	-24.773107	-38.322455	196.996090
H	-25.051781	-38.547122	198.512396
H	-28.062998	-39.930160	201.901942
H	-26.786422	-38.221525	199.827094
H	-26.742050	-39.261650	206.206228
H	-26.600932	-38.221681	205.058027
H	-25.772291	-45.791105	202.113448
H	-22.615309	-30.412855	207.621313
O	-28.981189	-30.166712	199.822721
H	-28.237194	-29.810162	200.343242
H	-28.516500	-30.693443	199.121816

REFERENCES

1. N. Ioannidis and V. Petrouleas, *Biochemistry*, 2000, **39**, 5246-5254.
2. A. Boussac, M. Sugiura, Y. Inoue and A. W. Rutherford, *Biochemistry*, 2000, **39**, 13788-13799.
3. Y. Sanakis, N. Ioannidis, G. Sioros and V. Petrouleas, *J. Am. Chem. Soc.*, 2001, **123**, 10766-10767.
4. J. H. A. Nugent, S. Turconi and M. C. W. Evans, *Biochemistry*, 1997, **36**, 7086-7096.