

Supporting information

Analyses of the electronic structures of FeFe-cofactors compared with FeMo- and FeV-cofactors and their P-clusters†

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Table S1 Bond valence analyses (abbreviated as Bval) for irons in FeFe-cofactor [1] in resting state (PDB entry: *8BOQ*).¹

Bond	r_{ij} (Å)	R_0 (Å)	B (Å)	Bval	Sum	Diff.	R_0 (Å)	B (Å)	Bval	Sum	Diff.
expected valence = +2						expected valence = +3					
Fe1–Scys	2.256	2.120	0.370	0.692			2.149	0.370	0.749		
Fe1–S1A	2.334	2.120	0.370	0.561			2.149	0.370	0.607		
Fe1–S2A	2.239	2.120	0.370	0.725			2.149	0.370	0.784		
Fe1–S4A	2.280	2.120	0.370	0.649	2.627	0.627	2.149	0.370	0.702	2.841	-0.159
Fe2–C	1.982	1.650	0.370	0.408			1.689	0.370	0.453		
Fe2–S1A	2.258	2.120	0.370	0.689			2.149	0.370	0.745		
Fe2–S2A	2.269	2.120	0.370	0.669			2.149	0.370	0.723		
Fe2–S2B	2.218	2.120	0.370	0.767	2.532	0.532	2.149	0.370	0.830	2.751	-0.249
Fe3–C	2.005	1.650	0.370	0.383			1.689	0.370	0.426		
Fe3–S2A	2.290	2.120	0.370	0.632			2.149	0.370	0.683		
Fe3–S4A	2.274	2.120	0.370	0.660			2.149	0.370	0.713		
Fe3–S5A	2.244	2.120	0.370	0.715	2.390	0.390	2.149	0.370	0.774	2.596	-0.404
Fe4–C	1.981	1.650	0.370	0.409			1.689	0.370	0.454		
Fe4–S1A	2.278	2.120	0.370	0.652			2.149	0.370	0.661		
Fe4–S3A	2.218	2.120	0.370	0.767			2.149	0.370	0.830		
Fe4–S4A	2.249	2.120	0.370	0.706	2.534	0.534	2.149	0.370	0.633	2.753	-0.247
Fe5–C	1.998	1.650	0.370	0.390			1.689	0.370	0.434		
Fe5–S1B	2.241	2.120	0.370	0.721			2.149	0.370	0.780		
Fe5–S3A	2.256	2.120	0.370	0.692			2.149	0.370	0.749		

Fe5-S4B	2.207	2.120	0.370	0.790	2.594	0.594	2.149	0.370	0.855	2.817	-0.183
Fe6-C	2.024	1.650	0.370	0.364			1.689	0.370	0.404		
Fe6-S1B	2.226	2.120	0.370	0.751			2.149	0.370	0.812		
Fe6-S2B	2.175	2.120	0.370	0.862			2.149	0.370	0.932		
Fe6-S3B	2.209	2.120	0.370	0.786	2.763	0.763	2.149	0.370	0.850	2.999	-0.001
Fe7-C	2.039	1.650	0.370	0.349			1.689	0.370	0.388		
Fe7-S3B	2.265	2.120	0.370	0.676			2.149	0.370	0.731		
Fe7-S4B	2.213	2.120	0.370	0.778			2.149	0.370	0.841		
Fe7-S5A	2.272	2.120	0.370	0.663	2.466	0.466	2.149	0.370	0.717	2.678	-0.322
Fe8-S1B	2.333	2.120	0.370	0.562			2.149	0.370	0.608		
Fe8-S3B	2.358	2.120	0.370	0.526			2.149	0.370	0.568		
Fe8-S4B	2.343	2.120	0.370	0.547			2.149	0.370	0.592		
Fe8-O5	2.078	1.734	0.370	0.395			1.759	0.370	0.422		
Fe8-O7	2.090	1.734	0.370	0.382			1.759	0.370	0.409		
Fe8-N	2.204	1.769	0.370	0.309	2.721	0.721	1.815	0.370	0.349	2.949	-0.051
					20.627	4.627				22.384	-1.616

Table S2 Bond valence analyses for irons in FeFe-cofactor [2] in resting state (PDB entry: *8BOQ*).¹

Bond	r_{ij} (Å)	R_0 (Å)	B (Å)	Bval	Sum	Diff.	R_0 (Å)	B (Å)	Bval	Sum	Diff.	
expected valence = +2							expected valence = +3					
Fe1–Scys	2.274	2.120	0.37	0.660			2.149	0.37	0.713			
Fe1–S1A	2.308	2.120	0.37	0.602			2.149	0.37	0.651			
Fe1–S2A	2.268	2.120	0.37	0.670			2.149	0.37	0.725			
Fe1–S4A	2.270	2.120	0.37	0.667	2.598	0.598	2.149	0.37	0.721	2.810	-0.190	
Fe2–C	1.994	1.650	0.37	0.395			1.689	0.37	0.439			
Fe2–S1A	2.295	2.120	0.37	0.623			2.149	0.37	0.674			
Fe2–S2A	2.239	2.120	0.37	0.725			2.149	0.37	0.784			
Fe2–S2B	2.211	2.120	0.37	0.782	2.525	0.525	2.149	0.37	0.846	2.742	-0.258	
Fe3–C	2.005	1.650	0.37	0.383			1.689	0.37	0.426			
Fe3–S2A	2.294	2.120	0.37	0.625			2.149	0.37	0.676			
Fe3–S4A	2.247	2.120	0.37	0.709			2.149	0.37	0.767			
Fe3–S5A	2.248	2.120	0.37	0.708	2.425	0.425	2.149	0.37	0.765	2.634	-0.366	
Fe4–C	1.992	1.650	0.37	0.397			1.689	0.37	0.441			
Fe4–S1A	2.278	2.120	0.37	0.652			2.149	0.37	0.706			
Fe4–S3A	2.240	2.120	0.37	0.723			2.149	0.37	0.782			
Fe4–S4A	2.249	2.120	0.37	0.706	2.478	0.478	2.149	0.37	0.763	2.692	-0.308	
Fe5–C	2.025	1.650	0.37	0.363			1.689	0.37	0.403			
Fe5–S1B	2.247	2.120	0.37	0.709			2.149	0.37	0.767			
Fe5–S3A	2.234	2.120	0.37	0.735			2.149	0.37	0.795			

Fe5-S4B	2.245	2.120	0.37	0.713	2.521	0.521	2.149	0.37	0.771	2.737	-0.263
Fe6-C	2.023	1.650	0.37	0.365			1.689	0.37	0.405		
Fe6-S1B	2.248	2.120	0.37	0.708			2.149	0.37	0.765		
Fe6-S3B	2.215	2.120	0.37	0.774			2.149	0.37	0.837		
Fe6-S2B	2.096	1.734	0.37	0.376	2.680	0.680	1.759	0.37	0.402	2.910	-0.090
Fe7-C	1.996	1.650	0.37	0.393			1.689	0.37	0.436		
Fe7-S3B	2.253	2.120	0.37	0.698			2.149	0.37	0.755		
Fe7-S4B	2.258	2.120	0.37	0.689			2.149	0.37	0.745		
Fe7-S5A	2.237	2.120	0.37	0.729	2.508	0.508	2.149	0.37	0.788	2.724	-0.276
Fe8-S1B	2.370	2.120	0.37	0.509			2.149	0.37	0.550		
Fe8-S3B	2.381	2.120	0.37	0.494			2.149	0.37	0.534		
Fe8-S4B	2.281	2.120	0.37	0.647			2.149	0.37	0.700		
Fe8-O5	2.364	1.734	0.37	0.182			1.759	0.37	0.195		
Fe8-O7	2.175	1.734	0.37	0.304			1.759	0.37	0.325		
Fe8-N	2.241	1.769	0.37	0.279	2.415	0.415	1.815	0.37	0.316	2.620	-0.380
					20.150	4.150				21.869	-2.131

Table S3 Bond valence analyses for irons in FeFe-cofactor [1] in turnover state (PDB entry: *8BOQ*).¹

Bond	r_{ij} (Å)	R_0 (Å)	B (Å)	Bval	Sum	Diff.	R_0 (Å)	B (Å)	Bval	Sum	Diff.
expected valence = +2						expected valence = +3					
Fe1–Scys	2.256	2.120	0.370	0.692			2.149	0.370	0.749		
Fe1–S1A	2.334	2.120	0.370	0.561			2.149	0.370	0.607		
Fe1–S2A	2.239	2.120	0.370	0.725			2.149	0.370	0.784		
Fe1–S4A	2.280	2.120	0.370	0.649	2.627	0.627	2.149	0.370	0.702	2.841	-0.159
Fe2–C	1.982	1.650	0.370	0.408			1.689	0.370	0.453		
Fe2–S1A	2.258	2.120	0.370	0.689			2.149	0.370	0.745		
Fe2–S2A	2.269	2.120	0.370	0.669			2.149	0.370	0.723		
Fe2–O	1.967	1.734	0.37	0.533	2.298	0.298	1.759	0.37	0.570	2.491	0.509
Fe3–C	2.005	1.650	0.370	0.383			1.689	0.370	0.426		
Fe3–S2A	2.290	2.120	0.370	0.632			2.149	0.370	0.683		
Fe3–S4A	2.274	2.120	0.370	0.660			2.149	0.370	0.713		
Fe3–S5A	2.244	2.120	0.370	0.715	2.390	0.390	2.149	0.370	0.774	2.596	-0.404
Fe4–C	1.981	1.650	0.370	0.409			1.689	0.370	0.454		
Fe4–S1A	2.278	2.120	0.370	0.652			2.149	0.370	0.661		
Fe4–S3A	2.218	2.120	0.370	0.767			2.149	0.370	0.830		
Fe4–S4A	2.249	2.120	0.370	0.706	2.534	0.534	2.149	0.370	0.633	2.753	-0.247
Fe5–C	1.998	1.650	0.370	0.390			1.689	0.370	0.434		
Fe5–S1B	2.241	2.120	0.370	0.721			2.149	0.370	0.780		
Fe5–S3A	2.256	2.120	0.370	0.692			2.149	0.370	0.749		
Fe5–S4B	2.207	2.120	0.370	0.790	2.594	0.594	2.149	0.370	0.855	2.817	-0.183

Fe6-C	2.024	1.650	0.370	0.364			1.689	0.370	0.404		
Fe6-S1B	2.226	2.120	0.370	0.751			2.149	0.370	0.812		
Fe6-S3B	2.209	2.120	0.370	0.786			2.149	0.370	0.850		
Fe6-O	1.962	1.734	0.37	0.540	2.441	0.441	1.759	0.37	0.578	2.645	0.355
Fe7-C	2.039	1.650	0.370	0.349			1.689	0.370	0.388		
Fe7-S3B	2.265	2.120	0.370	0.676			2.149	0.370	0.731		
Fe7-S4B	2.213	2.120	0.370	0.778			2.149	0.370	0.841		
Fe7-S5A	2.272	2.120	0.370	0.663	2.466	0.466	2.149	0.370	0.717	2.678	-0.322
Fe8-S1B	2.333	2.120	0.370	0.562			2.149	0.370	0.608		
Fe8-S3B	2.358	2.120	0.370	0.526			2.149	0.370	0.568		
Fe8-S4B	2.343	2.120	0.370	0.547			2.149	0.370	0.592		
Fe8-O5	2.078	1.734	0.370	0.395			1.759	0.370	0.422		
Fe8-O7	2.090	1.734	0.370	0.382			1.759	0.370	0.409		
Fe8-N	2.204	1.769	0.370	0.309	2.721	0.721	1.815	0.370	0.349	2.949	-0.051
					20.070	4.070				21.769	-2.231

Table S4 Bond valence analyses for irons in FeFe-cofactor [2] in turnover state (PDB entry: *8BOQ*).¹

Bond	r_{ij} (Å)	R_0 (Å)	B (Å)	Bval	Sum	Diff.	R_0 (Å)	B (Å)	Bval	Sum	Diff.
expected valence = +2						expected valence = +3					
Fe1–Scys	2.274	2.120	0.37	0.660			2.149	0.37	0.713		
Fe1–S1A	2.308	2.120	0.37	0.602			2.149	0.37	0.651		
Fe1–S2A	2.268	2.120	0.37	0.670			2.149	0.37	0.725		
Fe1–S4A	2.270	2.120	0.37	0.667	2.598	0.598	2.149	0.37	0.721	2.810	-0.190
Fe2–C	1.994	1.650	0.37	0.395			1.689	0.37	0.439		
Fe2–S1A	2.295	2.120	0.37	0.623			2.149	0.37	0.674		
Fe2–S2A	2.239	2.120	0.37	0.725			2.149	0.37	0.784		
Fe2–O	1.815	1.734	0.37	0.803	2.546	0.546	1.759	0.37	0.860	2.756	-0.244
Fe3–C	2.005	1.650	0.37	0.383			1.689	0.37	0.426		
Fe3–S2A	2.294	2.120	0.37	0.625			2.149	0.37	0.676		
Fe3–S4A	2.247	2.120	0.37	0.709			2.149	0.37	0.767		
Fe3–S5A	2.248	2.120	0.37	0.708	2.425	0.425	2.149	0.37	0.765	2.634	-0.366
Fe4–C	1.992	1.650	0.37	0.397			1.689	0.37	0.441		
Fe4–S1A	2.278	2.120	0.37	0.652			2.149	0.37	0.706		
Fe4–S3A	2.240	2.120	0.37	0.723			2.149	0.37	0.782		
Fe4–S4A	2.249	2.120	0.37	0.706	2.478	0.478	2.149	0.37	0.763	2.692	-0.308
Fe5–C	2.025	1.650	0.37	0.363			1.689	0.37	0.403		
Fe5–S1B	2.247	2.120	0.37	0.709			2.149	0.37	0.767		

Fe5-S3A	2.234	2.120	0.37	0.735			2.149	0.37	0.795		
Fe5-S4B	2.245	2.120	0.37	0.713	2.521	0.521	2.149	0.37	0.771	2.737	-0.263
Fe6-C	2.023	1.650	0.37	0.365			1.689	0.37	0.405		
Fe6-S1B	2.248	2.120	0.37	0.708			2.149	0.37	0.765		
Fe6-S3B	2.215	2.120	0.37	0.774			2.149	0.37	0.837		
Fe6-O	2.096	1.734	0.37	0.376	2.222	0.222	1.759	0.37	0.402	2.410	-0.590
Fe7-C	1.996	1.650	0.37	0.393			1.689	0.37	0.436		
Fe7-S3B	2.253	2.120	0.37	0.698			2.149	0.37	0.755		
Fe7-S4B	2.258	2.120	0.37	0.689			2.149	0.37	0.745		
Fe7-S5A	2.237	2.120	0.37	0.729	2.508	0.508	2.149	0.37	0.788	2.724	-0.276
Fe8-S1B	2.370	2.120	0.37	0.509			2.149	0.37	0.550		
Fe8-S3B	2.381	2.120	0.37	0.494			2.149	0.37	0.534		
Fe8-S4B	2.281	2.120	0.37	0.647			2.149	0.37	0.700		
Fe8-O5	2.364	1.734	0.37	0.182			1.759	0.37	0.195		
Fe8-O7	2.175	1.734	0.37	0.304			1.759	0.37	0.325		
Fe8-N	2.241	1.769	0.37	0.279	2.415	0.415	1.815	0.37	0.316	2.620	-0.380
					19.713	3.713				21.383	-2.617

Table S5 Bond valence analyses (abbreviated as Bval) for irons in FeFe-cofactor [1] in resting state (PDB entry: 8OIE).²

Bond	r_{ij} (Å)	R_0 (Å)	B (Å)	Bval	Sum	Diff.	R_0 (Å)	B (Å)	Bval	Sum	Diff.
expected valence = +2						expected valence = +3					
Fe1–Scys	2.254	2.120	0.370	0.696			2.149	0.370	0.753		
Fe1–S1A	2.268	2.120	0.370	0.610			2.149	0.370	0.725		
Fe1–S2A	2.280	2.120	0.370	0.670			2.149	0.370	0.702		
Fe1–S4A	2.303	2.120	0.370	0.649	2.625	0.625	2.149	0.370	0.660	2.839	-0.161
Fe2–C	1.986	1.650	0.370	0.376			1.689	0.370	0.448		
Fe2–S1A	2.265	2.120	0.370	0.713			2.149	0.370	0.731		
Fe2–S2A	2.248	2.120	0.370	0.834			2.149	0.370	0.765		
Fe2–S2B	2.221	2.120	0.370	0.692	2.616	0.616	2.149	0.370	0.823	2.767	-0.233
Fe3–C	2.003	1.650	0.370	0.403			1.689	0.370	0.428		
Fe3–S2A	2.280	2.120	0.370	0.676			2.149	0.370	0.702		
Fe3–S4A	2.280	2.120	0.370	0.708			2.149	0.370	0.702		
Fe3–S5A	2.234	2.120	0.370	0.761	2.548	0.548	2.149	0.370	0.795	2.626	-0.374
Fe4–C	2.012	1.650	0.370	0.385			1.689	0.370	0.418		
Fe4–S1A	2.245	2.120	0.370	0.649			2.149	0.370	0.771		
Fe4–S3A	2.187	2.120	0.370	0.649			2.149	0.370	0.902		
Fe4–S4A	2.256	2.120	0.370	0.735	2.418	0.418	2.149	0.370	0.749	2.840	-0.160
Fe5–C	2.003	1.650	0.370	0.390			1.689	0.370	0.428		
Fe5–S1B	2.214	2.120	0.370	0.700			2.149	0.370	0.839		
Fe5–S3A	2.167	2.120	0.370	0.708			2.149	0.370	0.953		
Fe5–S4B	2.219	2.120	0.370	0.700	2.498	0.498	2.149	0.370	0.828	3.047	0.047

Fe6-C	1.975	1.650	0.370	0.385			1.689	0.370	0.462		
Fe6-S1B	2.244	2.120	0.370	0.765			2.149	0.370	0.774		
Fe6-S2B	2.207	2.120	0.370	0.881			2.149	0.370	0.855		
Fe6-S3B	2.207	2.120	0.370	0.776	2.807	0.807	2.149	0.370	0.855	2.945	-0.055
Fe7-C	1.998	1.650	0.370	0.415			1.689	0.370	0.434		
Fe7-S3B	2.252	2.120	0.370	0.715			2.149	0.370	0.757		
Fe7-S4B	2.252	2.120	0.370	0.790			2.149	0.370	0.757		
Fe7-S5A	2.248	2.120	0.370	0.790	2.712	0.712	2.149	0.370	0.765	2.713	-0.287
Fe8-S1B	2.272	2.120	0.370	0.607			2.149	0.370	0.717		
Fe8-S3B	2.292	2.120	0.370	0.663			2.149	0.370	0.679		
Fe8-S4B	2.305	2.120	0.370	0.628			2.149	0.370	0.656		
Fe8-O5	2.208	1.734	0.370	0.278			1.759	0.370	0.297		
Fe8-O7	2.202	1.734	0.370	0.282			1.759	0.370	0.302		
Fe8-N	2.712	1.769	0.370	0.078	2.536	0.536	1.815	0.370	0.089	2.740	-0.260
					20.759	4.759				22.519	-1.481

Table S6 Bond valence analyses (abbreviated as Bval) for irons in FeFe-cofactor [2] in resting state (PDB entry: 8OIE).²

Bond	r_{ij} (Å)	R_0 (Å)	B (Å)	Bval	Sum	Diff.	R_0 (Å)	B (Å)	Bval	Sum	Diff.
expected valence = +2						expected valence = +3					
Fe1–Scys	2.262	2.120	0.370	0.681			2.149	0.370	0.737		
Fe1–S1A	2.306	2.120	0.370	1.376			2.149	0.370	0.654		
Fe1–S2A	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe1–S4A	2.274	2.120	0.370	0.660	3.358	1.358	2.149	0.370	0.713	2.799	-0.201
Fe2–C	2.002	1.650	0.370	0.386			1.689	0.370	0.429		
Fe2–S1A	2.260	2.120	0.370	0.685			2.149	0.370	0.741		
Fe2–S2A	2.253	2.120	0.370	0.698			2.149	0.370	0.755		
Fe2–S2B	2.252	2.120	0.370	0.700	2.469	0.469	2.149	0.370	0.757	2.682	-0.318
Fe3–C	1.980	1.650	0.370	0.410			1.689	0.370	0.455		
Fe3–S2A	2.214	2.120	0.370	0.776			2.149	0.370	0.839		
Fe3–S4A	2.243	2.120	0.370	0.717			2.149	0.370	0.776		
Fe3–S5A	2.207	2.120	0.370	0.790	2.693	0.693	2.149	0.370	0.855	2.925	-0.075
Fe4–C	2.004	1.650	0.370	0.384			1.689	0.370	0.427		
Fe4–S1A	2.233	2.120	0.370	0.737			2.149	0.370	0.797		
Fe4–S3A	2.170	2.120	0.370	0.874			2.149	0.370	0.945		
Fe4–S4A	2.213	2.120	0.370	0.778	2.772	0.772	2.149	0.370	0.841	3.010	0.010
Fe5–C	2.010	1.650	0.370	0.378			1.689	0.370	0.420		
Fe5–S1B	2.257	2.120	0.370	0.691			2.149	0.370	0.747		
Fe5–S3A	2.185	2.120	0.370	0.839			2.149	0.370	0.907		
Fe5–S4B	2.232	2.120	0.370	0.739	2.646	0.646	2.149	0.370	0.799	2.873	-0.127

Fe6-C	1.998	1.650	0.370	0.390			1.689	0.370	0.434		
Fe6-S1B	2.280	2.120	0.370	0.649			2.149	0.370	0.702		
Fe6-S2B	2.235	2.120	0.370	0.733			2.149	0.370	0.793		
Fe6-S3B	2.275	2.120	0.370	0.658	2.430	0.430	2.149	0.370	0.711	2.640	-0.360
Fe7-C	1.984	1.650	0.370	0.405			1.689	0.370	0.451		
Fe7-S3B	2.248	2.120	0.370	0.708			2.149	0.370	0.765		
Fe7-S4B	2.260	2.120	0.370	0.685			2.149	0.370	0.741		
Fe7-S5A	2.216	2.120	0.370	0.771	2.569	0.569	2.149	0.370	0.834	2.791	-0.209
Fe8-S1B	2.303	2.120	0.370	0.610			2.149	0.370	0.660		
Fe8-S3B	2.288	2.120	0.370	0.635			2.149	0.370	0.687		
Fe8-S4B	2.269	2.120	0.370	0.669			2.149	0.370	0.723		
Fe8-O5	2.214	1.734	0.370	0.273			1.759	0.370	0.292		
Fe8-O7	2.203	1.734	0.370	0.282			1.759	0.370	0.301		
Fe8-N	2.709	1.769	0.370	0.079	2.547	0.547	1.815	0.370	0.089	2.752	-0.248
					21.486	5.486				22.471	-1.529

Table S7 Bond valence analyses for irons in P^N cluster [1] from FeFe-protein (PDB entry: *8BOQ*).¹

Bond	r_{ij} (Å)	R_0 (Å)	B (Å)	Bval	Sum	Diff.	R_0 (Å)	B (Å)	Bval	Sum	Diff.
expected valence = +2						expected valence = +3					
Fe1-S1	2.395	2.120	0.370	0.476			2.149	0.370	0.514		
Fe1-S2A	2.311	2.120	0.370	0.597			2.149	0.370	0.645		
Fe1-S3A	2.328	2.120	0.370	0.570			2.149	0.370	0.616		
Fe1-SG	2.287	2.120	0.370	0.637	2.279	0.279	2.149	0.370	0.689	2.465	-0.535
Fe2-S1	2.461	2.120	0.370	0.398			2.149	0.370	0.430		
Fe2-S2A	2.291	2.120	0.370	0.630			2.149	0.370	0.681		
Fe2-S4A	2.346	2.120	0.370	0.543			2.149	0.370	0.587		
Fe2-SG	2.364	2.120	0.370	0.517	2.088	0.088	2.149	0.370	0.559	2.258	-0.742
Fe3-S2A	2.294	2.120	0.370	0.625			2.149	0.370	0.676		
Fe3-S3A	2.310	2.120	0.370	0.598			2.149	0.370	0.647		
Fe3-S4A	2.236	2.120	0.370	0.731			2.149	0.370	0.790		
Fe3-SG	2.263	2.120	0.370	0.679	2.634	0.634	2.149	0.370	0.735	2.848	-0.152
Fe4-S1	2.463	2.120	0.370	0.396			2.149	0.370	0.428		
Fe4-S3A	2.295	2.120	0.370	0.623			2.149	0.370	0.674		
Fe4-S4A	2.258	2.120	0.370	0.689			2.149	0.370	0.745		
Fe4-SG	2.229	2.120	0.370	0.745	2.452	0.452	2.149	0.370	0.806	2.652	-0.348
Fe5-S1	2.476	2.120	0.370	0.382			2.149	0.370	0.413		
Fe5-S2B	2.367	2.120	0.370	0.513			2.149	0.370	0.555		
Fe5-S4B	2.279	2.120	0.370	0.651			2.149	0.370	0.704		
Fe5-SG	2.309	2.120	0.370	0.600	2.146	0.146	2.149	0.370	0.649	2.321	-0.679
Fe6-S1	2.554	2.120	0.370	0.309			2.149	0.370	0.335		
Fe6-S2B	2.461	2.120	0.370	0.398			2.149	0.370	0.430		
Fe6-S3B	2.299	2.120	0.370	0.616			2.149	0.370	0.667		

Fe6-SG	2.342	2.120	0.370	0.549	1.873	-0.127	2.149	0.370	0.594	2.025	-0.975
Fe7-S2B	2.354	2.120	0.370	0.531			2.149	0.370	0.575		
Fe7-S3B	2.277	2.120	0.370	0.654			2.149	0.370	0.708		
Fe7-S4B	2.251	2.120	0.370	0.702			2.149	0.370	0.759		
Fe7-SG	2.357	2.120	0.370	0.527	2.414	0.414	2.149	0.370	0.570	2.611	-0.389
Fe8-S1	2.361	2.120	0.370	0.521			2.149	0.370	0.564		
Fe8-S3B	2.259	2.120	0.370	0.687			2.149	0.370	0.743		
Fe8-S4B	2.294	2.120	0.370	0.625			2.149	0.370	0.676		
Fe8-SG	2.293	2.120	0.370	0.627	2.460	0.460	2.149	0.370	0.678	2.660	-0.340
					18.345	2.345				19.841	-4.159

Table S8 Bond valence analyses for irons in P^N cluster [2] from FeFe-protein (PDB entry: *8BOQ*).¹

Bond	r_{ij} (Å)	R_0 (Å)	B (Å)	Bval	Sum	Diff.	R_0 (Å)	B (Å)	Bval	Sum	Diff.
expected valence = +2						expected valence = +3					
Fe1-S1	2.429	2.120	0.370	0.434			2.149	0.370	0.469		
Fe1-S2A	2.292	2.120	0.370	0.628			2.149	0.370	0.679		
Fe1-S3A	2.307	2.120	0.370	0.603			2.149	0.370	0.652		
Fe1-SG	2.457	2.120	0.370	0.402	2.067	0.067	2.149	0.370	0.435	2.236	-0.764
Fe2-S1	2.456	2.120	0.370	0.403			2.149	0.370	0.436		
Fe2-S2A	2.307	2.120	0.370	0.603			2.149	0.370	0.652		
Fe2-S4A	2.327	2.120	0.370	0.572			2.149	0.370	0.618		
Fe2-SG	2.291	2.120	0.370	0.630	2.208	0.208	2.149	0.370	0.681	2.388	-0.612
Fe3-S2A	2.305	2.120	0.370	0.607			2.149	0.370	0.656		
Fe3-S3A	2.365	2.120	0.370	0.516			2.149	0.370	0.558		
Fe3-S4A	2.228	2.120	0.370	0.747			2.149	0.370	0.808		
Fe3-SG	2.273	2.120	0.370	0.661	2.530	0.530	2.149	0.370	0.715	2.737	-0.263
Fe4-S1	2.421	2.120	0.370	0.443			2.149	0.370	0.479		
Fe4-S3A	2.303	2.120	0.370	0.610			2.149	0.370	0.660		
Fe4-S4A	2.317	2.120	0.370	0.587			2.149	0.370	0.635		
Fe4-SG	2.250	2.120	0.370	0.704	2.344	0.344	2.149	0.370	0.761	2.535	-0.465
Fe5-S1	2.507	2.120	0.370	0.351			2.149	0.370	0.380		
Fe5-S2B	2.371	2.120	0.370	0.507			2.149	0.370	0.549		
Fe5-S4B	2.266	2.120	0.370	0.674			2.149	0.370	0.729		
Fe5-SG	2.231	2.120	0.370	0.741	2.274	0.274	2.149	0.370	0.801	2.459	-0.541
Fe6-S1	2.588	2.120	0.370	0.282			2.149	0.370	0.305		
Fe6-S2B	2.491	2.120	0.370	0.367			2.149	0.370	0.397		

Fe6-S3B	2.253	2.120	0.370	0.698			2.149	0.370	0.755		
Fe6-SG	2.352	2.120	0.370	0.534	1.881	-0.119	2.149	0.370	0.578	2.035	-0.965
Fe7-S2B	2.320	2.120	0.370	0.582			2.149	0.370	0.630		
Fe7-S3B	2.324	2.120	0.370	0.576			2.149	0.370	0.623		
Fe7-S4B	2.247	2.120	0.370	0.709			2.149	0.370	0.767		
Fe7-SG	2.333	2.120	0.370	0.562	2.430	0.430	2.149	0.370	0.608	2.629	-0.371
Fe8-S1	2.363	2.120	0.370	0.519			2.149	0.370	0.561		
Fe8-S3B	2.250	2.120	0.370	0.704			2.149	0.370	0.761		
Fe8-S4B	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe8-SG	2.275	2.120	0.370	0.658	2.532	0.532	2.149	0.370	0.711	2.739	-0.261
					18.354	2.354				19.850	-4.150

Table S9 Bond valence analyses for irons in P^N cluster [1] from FeFe-protein (PDB entry: 8OIE).²

Bond	r_{ij} (Å)	R_0 (Å)	B (Å)	Bval	Sum	Diff.	R_0 (Å)	B (Å)	Bval	Sum	Diff.
expected valence = +2						expected valence = +3					
Fe1-S1	2.497	2.120	0.370	0.361			2.149	0.370	0.390		
Fe1-S2A	2.316	2.120	0.370	0.589			2.149	0.370	0.637		
Fe1-S3A	2.359	2.120	0.370	0.524			2.149	0.370	0.567		
Fe1-SG	2.241	2.120	0.370	0.721	2.195	0.195	2.149	0.370	0.780	2.374	-0.626
Fe2-S1	2.428	2.120	0.370	0.435			2.149	0.370	0.470		
Fe2-S2A	2.312	2.120	0.370	0.595			2.149	0.370	0.644		
Fe2-S4A	2.251	2.120	0.370	0.702			2.149	0.370	0.759		
Fe2-SG	2.330	2.120	0.370	0.567	2.299	0.299	2.149	0.370	0.613	2.486	-0.514
Fe3-S2A	2.366	2.120	0.370	0.514			2.149	0.370	0.556		
Fe3-S3A	2.341	2.120	0.370	0.550			2.149	0.370	0.595		
Fe3-S4A	2.373	2.120	0.370	0.505			2.149	0.370	0.546		
Fe3-SG	2.299	2.120	0.370	0.616	2.186	0.186	2.149	0.370	0.667	2.364	-0.636
Fe4-S1	2.480	2.120	0.370	0.378			2.149	0.370	0.409		
Fe4-S3A	2.370	2.120	0.370	0.509			2.149	0.370	0.550		
Fe4-S4A	2.222	2.120	0.370	0.759			2.149	0.370	0.821		
Fe4-SG	2.248	2.120	0.370	0.708	2.353	0.353	2.149	0.370	0.765	2.545	-0.455
Fe5-S1	2.479	2.120	0.370	0.379			2.149	0.370	0.410		
Fe5-S2B	2.290	2.120	0.370	0.632			2.149	0.370	0.683		
Fe5-S4B	2.266	2.120	0.370	0.674			2.149	0.370	0.729		
Fe5-SG	2.251	2.120	0.370	0.702	2.386	0.386	2.149	0.370	0.759	2.581	-0.419
Fe6-S1	2.405	2.120	0.370	0.463			2.149	0.370	0.501		
Fe6-S2B	2.315	2.120	0.370	0.590			2.149	0.370	0.638		
Fe6-S3B	2.266	2.120	0.370	0.670			2.149	0.370	0.729		

Fe6-SG	2.268	2.120	0.370	0.670	2.394	0.394	2.149	0.370	0.725	2.593	-0.407
Fe7-S2B	2.319	2.120	0.370	0.584			2.149	0.370	0.632		
Fe7-S3B	2.375	2.120	0.370	0.502			2.149	0.370	0.543		
Fe7-S4B	2.282	2.120	0.370	0.645			2.149	0.370	0.698		
Fe7-SG	2.238	2.120	0.370	0.727	2.458	0.458	2.149	0.370	0.786	2.659	-0.341
Fe8-S1	2.393	2.120	0.370	0.478			2.149	0.370	0.517		
Fe8-S3B	2.231	2.120	0.370	0.741			2.149	0.370	0.801		
Fe8-S4B	2.267	2.120	0.370	0.672			2.149	0.370	0.727		
Fe8-SG	2.280	2.120	0.370	0.649	2.540	0.540	2.149	0.370	0.702	2.747	-0.253
					18.812	2.812				20.349	-3.651

Table S10 Bond valence analyses for irons in P^N cluster [2] from FeFe-protein (PDB entry: *8OIE*).²

Bond	r_{ij} (Å)	R_0 (Å)	B (Å)	Bval	Sum	Diff.	R_0 (Å)	B (Å)	Bval	Sum	Diff.
expected valence = +2						expected valence = +3					
Fe1-S1	2.399	2.120	0.370	0.470			2.149	0.370	0.509		
Fe1-S2A	2.317	2.120	0.370	0.587			2.149	0.370	0.635		
Fe1-S3A	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe1-SG	2.399	2.120	0.370	0.470	2.189	0.189	2.149	0.370	0.509	2.368	-0.632
Fe2-S1	2.490	2.120	0.370	0.368			2.149	0.370	0.398		
Fe2-S2A	2.294	2.120	0.370	0.625			2.149	0.370	0.676		
Fe2-S4A	2.270	2.120	0.370	0.667			2.149	0.370	0.721		
Fe2-SG	2.329	2.120	0.370	0.568	2.228	0.228	2.149	0.370	0.615	2.409	-0.591
Fe3-S2A	2.328	2.120	0.370	0.570			2.149	0.370	0.616		
Fe3-S3A	2.386	2.120	0.370	0.487			2.149	0.370	0.527		
Fe3-S4A	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe3-SG	2.311	2.120	0.370	0.597	2.291	0.291	2.149	0.370	0.645	2.478	-0.522
Fe4-S1	2.389	2.120	0.370	0.483			2.149	0.370	0.523		
Fe4-S3A	2.225	2.120	0.370	0.753			2.149	0.370	0.814		
Fe4-S4A	2.266	2.120	0.370	0.674			2.149	0.370	0.729		
Fe4-SG	2.249	2.120	0.370	0.706	2.616	0.616	2.149	0.370	0.763	2.829	-0.171
Fe5-S1	2.420	2.120	0.370	0.444			2.149	0.370	0.481		
Fe5-S2B	2.309	2.120	0.370	0.600			2.149	0.370	0.649		
Fe5-S4B	2.244	2.120	0.370	0.715			2.149	0.370	0.774		
Fe5-SG	2.257	2.120	0.370	0.691	2.450	0.450	2.149	0.370	0.747	2.650	-0.350
Fe6-S1	2.507	2.120	0.370	0.674			2.149	0.370	0.380		
Fe6-S2B	2.319	2.120	0.370	0.584			2.149	0.370	0.632		
Fe6-S3B	2.351	2.120	0.370	0.536			2.149	0.370	0.579		

Fe6-SG	2.266	2.120	0.370	0.674	2.468	0.468	2.149	0.370	0.729	2.320	-0.680
Fe7-S2B	2.357	2.120	0.370	0.527			2.149	0.370	0.570		
Fe7-S3B	2.331	2.120	0.370	0.565			2.149	0.370	0.611		
Fe7-S4B	2.368	2.120	0.370	0.512			2.149	0.370	0.553		
Fe7-SG	2.230	2.120	0.370	0.743	2.347	0.347	2.149	0.370	0.803	2.538	-0.462
Fe8-S1	2.484	2.120	0.370	0.374			2.149	0.370	0.404		
Fe8-S3B	2.377	2.120	0.370	0.499			2.149	0.370	0.540		
Fe8-S4B	2.223	2.120	0.370	0.757			2.149	0.370	0.819		
Fe8-SG	2.282	2.120	0.370	0.645	2.276	0.276	2.149	0.370	0.698	2.461	-0.539
					18.864	2.864				20.053	-3.947

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