Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Statistical analysis of P^N clusters in Mo/VFe protein crystals using a bond valence method toward their electronic structures

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Table Options

Figure S1 The curves of w_i by adopting different P in P-clusters of MoFe proteins along with different resolutions.

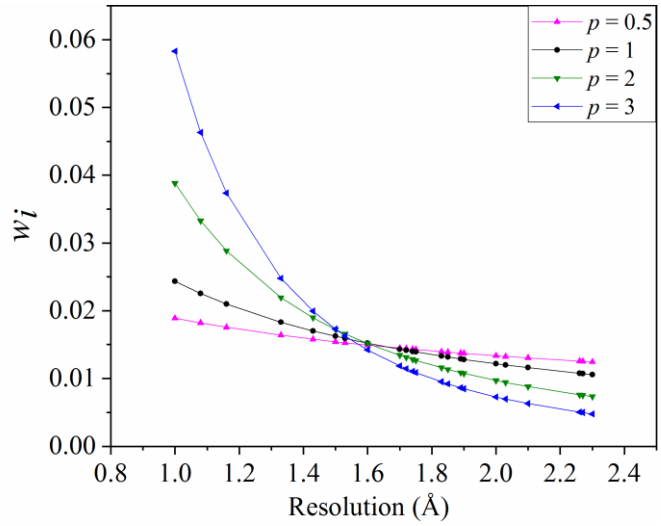

Table S1 The averaged deviations d ($d=S_i - n$, n= +2 and +3) of P^N clusters in **adopted** PDB entries by using R_0 (+2) and R_0 (+3).

PDB codes	Number of P-clusters	Res (Å)	Averaged d by using R_0 (+2)									Averaged d by using R_0 (+3)								
			Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7	Fe8	8Fe	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7	Fe8	8Fe
Adopted P^N in MoFe proteins																				
3U7Q	2	1.00	0.271	0.199	0.530	0.363	0.118	-0.118	0.313	0.354	2.030	-0.544	-0.621	-0.264	-0.444	-0.710	-0.965	-0.499	-0.454	-4.500
4WES	2	1.08	0.212	0.135	0.420	0.275	0.064	-0.151	0.369	0.359	1.684	-0.607	-0.691	-0.383	-0.540	-0.767	-1.000	-0.437	-0.449	-4.874
1M1N	4	1.16	0.219	0.223	0.439	0.367	0.203	0.092	0.270	0.290	2.104	-0.600	-0.595	-0.362	-0.440	-0.617	-0.738	-0.545	-0.523	-4.420
7JRF	2	1.33	0.187	0.208	0.443	0.345	0.132	0.097	0.208	0.265	1.884	-0.635	-0.612	-0.357	-0.464	-0.695	-0.732	-0.612	-0.551	-4.658
4TKU	2	1.43	0.285	0.238	0.550	0.381	0.261	0.146	0.241	0.304	2.406	-0.529	-0.579	-0.242	-0.425	-0.555	-0.680	-0.576	-0.508	-4.094
4TKV	2	1.50	0.335	0.338	0.597	0.395	0.320	0.139	0.283	0.329	2.736	-0.475	-0.472	-0.191	-0.409	-0.491	-0.686	-0.531	-0.481	-3.736
5BVH	2	1.53	0.239	0.307	0.542	0.367	0.224	0.148	0.278	0.298	2.401	-0.579	-0.505	-0.251	-0.440	-0.595	-0.677	-0.537	-0.515	-4.099
1QGU	2	1.60	0.127	0.119	0.216	0.251	0.118	0.072	0.148	0.245	1.296	-0.700	-0.708	-0.603	-0.566	-0.710	-0.759	-0.677	-0.572	-5.294
1QH8	2	1.60	0.154	0.154	0.330	0.285	0.116	-0.033	0.325	0.439	1.771	-0.670	-0.670	-0.480	-0.528	-0.712	-0.872	-0.485	-0.362	-4.780
5BVG	2	1.60	0.175	0.307	0.572	0.377	0.296	0.132	0.329	0.300	2.488	-0.825	-0.693	-0.428	-0.623	-0.704	-0.868	-0.671	-0.700	-5.512
6OP3	2	1.60	0.566	0.503	0.722	0.694	0.216	0.087	0.157	0.279	3.225	-0.225	-0.293	-0.056	-0.087	-0.604	-0.742	-0.667	-0.535	-3.208
6O7P	2	1.70	0.322	0.353	0.636	0.310	0.545	0.172	0.262	0.286	2.886	-0.488	-0.455	-0.149	-0.501	-0.247	-0.651	-0.554	-0.528	-3.574
5VQ3	2	1.72	0.210	0.189	0.444	0.360	0.154	0.048	0.381	0.303	2.088	-0.610	-0.632	-0.357	-0.448	-0.670	-0.785	-0.425	-0.509	-4.437
6VXT	2	1.74	0.270	0.070	0.173	0.331	0.309	-0.037	0.005	0.026	1.146	-0.545	-0.762	-0.651	-0.479	-0.503	-0.877	-0.832	-0.809	-5.456
5CX1	8	1.75	0.310	0.363	0.520	0.300	0.217	0.128	0.333	0.295	2.465	-0.502	-0.445	-0.274	-0.513	-0.602	-0.699	-0.477	-0.518	-4.030
5KOH	2	1.83	0.231	0.322	0.544	0.417	0.194	0.104	0.356	0.298	2.466	-0.587	-0.489	-0.248	-0.386	-0.627	-0.724	-0.452	-0.515	-4.028
5VPW	2	1.85	0.269	0.274	0.443	0.391	0.092	-0.099	0.293	0.225	1.888	-0.546	-0.540	-0.357	-0.414	-0.738	-0.944	-0.520	-0.594	-4.653
6O7O	2	1.89	0.334	0.307	0.483	0.425	0.385	0.178	0.470	0.246	2.827	-0.476	-0.505	-0.315	-0.377	-0.421	-0.644	-0.329	-0.571	-3.638
1H1L	2	1.90	0.089	0.187	0.416	0.390	0.056	0.002	0.177	0.232	1.548	-0.741	-0.635	-0.387	-0.416	-0.777	-0.835	-0.646	-0.586	-5.022
4WZA	2	1.90	0.102	0.079	0.281	0.285	0.170	-0.006	0.032	0.189	1.133	-0.726	-0.751	-0.533	-0.529	-0.653	-0.843	-0.802	-0.633	-5.470
4WZB	2	1.90	0.151	-0.018	0.246	0.231	0.120	-0.127	0.025	0.107	0.734	-0.674	-0.857	-0.571	-0.587	-0.707	-0.974	-0.810	-0.721	-5.901
4WNA	2	2.00	0.161	0.326	0.664	0.589	0.187	-0.060	0.387	0.438	2.693	-0.663	-0.485	-0.118	-0.200	-0.634	-0.902	-0.418	-0.363	-3.783
6O7Q	2	2.00	0.094	0.248	0.552	0.189	0.309	-0.088	0.263	0.321	1.889	-0.735	-0.569	-0.240	-0.633	-0.502	-0.932	-0.552	-0.490	-4.653
3MIN	2	2.03	0.851	0.430	0.816	0.909	0.581	0.122	0.542	0.421	4.673	0.084	-0.372	0.046	0.147	-0.208	-0.705	-0.251	-0.382	-1.641
2AFH	2	2.10	0.817	0.053	0.679	1.039	0.991	0.116	0.432	0.979	5.106	0.047	-0.780	-0.102	0.287	0.235	-0.711	-0.370	0.222	-1.174
6O7L	2	2.26	0.209	0.271	0.795	0.461	0.654	0.206	-0.234	0.430	2.792	-0.610	-0.544	0.023	-0.339	-0.130	-0.615	-1.090	-0.372	-3.676
6O7R	2	2.27	0.331	0.440	0.765	0.490	0.463	0.134	0.335	0.646	3.603	-0.479	-0.361	-0.009	-0.307	-0.337	-0.692	-0.475	-0.138	-2.799
1L5H	1	2.30	0.815	0.552	0.367	0.297	0.258	-0.217	0.541	0.402	3.015	0.045	-0.240	-0.440	-0.515	-0.558	-1.072	-0.252	-0.402	-3.435
1M34	4	2.30	0.495	0.558	0.561	0.656	0.240	-0.011	0.467	0.321	3.287	-0.302	-0.234	-0.230	-0.127	-0.577	-0.849	-0.332	-0.489	-3.141
5VQ4	2	2.30	0.122	0.262	0.597	0.488	0.040	-0.264	0.293	0.461	1.999	-0.705	-0.554	-0.192	-0.309	-0.794	-1.122	-0.520	-0.339	-4.534
Adopted P^N in VFe proteins																				
5N6Y	2	1.35	0.221	0.155	0.384	0.296	0.280	0.145	0.480	0.446	2.407	-0.598	-0.669	-0.422	-0.517	-0.534	-0.680	-0.318	-0.355	-4.092
6FEA	2	1.20	0.168	0.105	0.364	0.307	0.233	0.059	0.447	0.406	2.089	-0.655	-0.723	-0.444	-0.505	-0.585	-0.773	-0.353	-0.398	-4.436
7ADR	2	1.00	0.146	0.083	0.319	0.277	0.193	0.067	0.401	0.368	1.854	-0.680	-0.747	-0.491	-0.537	-0.628	-0.765	-0.404	-0.439	-4.690
7ADY	2	1.05	0.145	0.075	0.323	0.271	0.173	0.053	0.400	0.349	1.789	-0.680	-0.755	-0.488	-0.544	-0.650	-0.779	-0.405	-0.459	-4.761
7AIZ	2	1.05	0.160	0.075	0.306	0.282	0.173	0.035	0.409	0.338	1.777	-0.664	-0.755	-0.506	-0.532	-0.650	-0.799	-0.395	-0.471	-4.772

Table S2 The averaged d ($d=S_i - n$, $n= +2$ and $+3$) of P^N clusters in **abandoned** PDB entries by using R_0 (+2) and R_0 (+3), and the reasons that they were not taken into BVS analysis are listed below. Blank items on account of that the corresponding values are improper to present. Special illustration of PDB entries that perform as P^{1+}, P^{2+}, and mixed state $P^{N/1+}$, $P^{1+/2+}$ and $P^{N/2+}$ are classified too.

PDB codes	Number of P-clusters	Res (Å)	Averaged d by using R_0 (+2)									Averaged d by using R_0 (+3)								
			Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7	Fe8	8Fe	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7	Fe8	8Fe
Abandoned P^N in MoFe proteins：																				
P^N clusters of wrong [Fe_8S_8] structures																				
1MIO	2	3.00	0.491	0.547	0.408	0.418	0.367	0.732	0.289	0.426		-0.306	-0.246	-0.396	-0.385	-0.440	-0.042	-0.525	-0.376	
P^N clusters without valid Fe3 and Fe7–S_{cys} bonds																				
3K1A	2	2.23	0.273	1.558		1.306	1.139	0.705		1.626		-0.543	0.848		0.575	0.395	-0.075		0.921	
P^N clusters without Fe1 and Fe5 substituted by Na atom																				
6O7S	2	2.27		0.310	0.580	0.389		-0.079	0.334	0.466			-0.502	-0.210	-0.417		-0.923	-0.477	-0.333	
P^N clusters which have overlarge calculated bond valences due to its resolutions beyond 2.3 Å																				
1M1Y	4	3.20	0.833	0.430	1.088	2.367	1.674	0.323	0.097	1.231	8.042	0.064	-0.372	0.340	1.723	0.973	-0.487	-0.732	0.494	2.003
2AFI	4	3.10	1.153	0.360	0.974	1.488	1.188	0.443	0.807	1.320	7.733	0.410	-0.448	0.217	0.772	0.448	-0.357	0.036	0.591	1.669
P^N clusters which have too short Fe-S bond lead to weird bond valences in several Fe atoms																				
6BBL	2	1.68	0.709	0.658	0.929	0.704	0.619	0.350	0.772	0.652	5.394	-0.070	-0.126	0.168	-0.076	-0.168	-0.458	-0.002	-0.131	-0.862
6OP1	2	1.70	1.018	0.726	1.068	0.992	0.224	0.093	0.198	0.292	4.612	0.264	-0.051	0.318	0.236	-0.595	-0.736	-0.622	-0.521	-1.707
6OP2	2	1.90	1.507	1.060	1.734	1.614	0.285	-0.055	0.182	0.286	6.612	0.793	0.310	1.039	0.909	-0.529	-0.897	-0.641	-0.528	0.455
6OP4	2	2.30	3.545	1.338	1.879	1.852	0.366	-0.033	0.288	0.557	9.793	2.997	0.611	1.195	1.166	-0.441	-0.872	-0.525	-0.234	3.896
other special P-clusters in MoFe proteins：																				
Unclear $P^{N/1+}$ (regarded as P^N or adopted the part of P^N): 1M34、5CX1、5VQ4、6BBL(abandoned)																				
Unclear $P^{1+/2+}$: 1N2C、1FP4																				
$P^{N/2+}$ superposition: 1QH8、3U7Q、4WES、4WNA																				
Unclear P^{1+}: 6CDK																				
P^{2+}: 1G20、1QH1、2MIN、4ND8、4WN9、4XPI、6O7M、6UG0																				
Dubious P^{2+}: 1FP4、1G21																				
Mutant P^{2+} clusters (Fe8–O instead of Fe6–O): 5KOJ、6O7N																				
Superposed state $P^{N/1+}$ clusters in VFe proteins：																				
Unclear $P^{N/1+}$ (adopted the part of P^N): 6FEA、7ADR、7ADY、7AIZ																				

Table S3 The abandoned bond valence sums (abbreviated as Bval) of iron atoms in P^N clusters which contain unreasonable structures and faulty data. Blank items present the valence of irons which are improper to be calculated due to unreasonable structures. Apparent faulty data in R_0 (+2) are bold highlighted. Further detail calculations of abandoned PDB entries are listed below Table S4 to Table S25.

PDB code	Resolution (Å)	**Bval by using R_0(+2)**									**Bval by using R_0(+3)**								
		Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7	Fe8	8Fe	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7	Fe8	8Fe
P-cluster with unreasonable structure																			
1MIO[2]	3.00			2.423				2.272					2.620				2.457		
				2.393				2.305					2.588				2.493		
3K1A[4]	2.23	2.244	**3.502**		**3.354**	3.015	2.614		**3.643**		2.426	3.788		3.627	3.261	2.827		3.940	
		2.301	**3.614**		**3.257**	**3.263**	2.796		**3.608**		2.488	3.908		3.523	3.529	3.024		3.902	
6O7S[5]	2.27		2.355	2.599	2.368		1.917	2.370	2.441			2.547	2.811	2.561		2.073	2.563	2.640	
			2.265	2.561	2.409		1.924	2.297	2.491			2.449	2.770	2.605		2.081	2.484	2.694	
P-cluster with faulty data																			
1M1Y[6]	3.20	2.444	2.491	**3.459**	**4.768**	**3.762**	2.197	1.962	**3.231**	**24.314**	2.643	2.694	3.741	5.157	4.069	2.376	2.121	3.494	26.297
		2.715	2.352	3.026	**3.819**	**3.272**	2.299	2.032	**3.477**	22.993	2.937	2.544	3.273	4.131	3.539	2.487	2.197	3.761	24.868
		3.078	2.560	3.098	**5.553**	**4.466**	2.484	2.401	**3.391**	**27.030**	3.329	2.768	3.351	6.006	4.830	2.686	2.596	3.667	29.233
		3.096	2.316	2.769	**3.326**	**3.195**	2.313	1.993	2.824	21.832	3.348	2.505	2.994	3.598	3.455	2.501	2.156	3.055	23.612
2AFI[7]	3.10	2.965	2.318	2.966	**3.510**	**3.225**	2.434	2.758	**3.293**	23.470	3.207	2.508	3.207	3.796	3.488	2.633	2.983	3.562	25.383
		3.033	2.358	3.003	**3.334**	**3.179**	2.480	2.820	**3.324**	23.532	3.281	2.551	3.248	3.606	3.438	2.682	3.050	3.595	25.451

		3.390	2.516	2.938	**3.727**	**3.211**	2.495	2.829	**3.362**	**24.468**	3.667	2.722	3.177	4.031	3.472	2.699	3.060	3.636	26.463
		3.224	2.247	2.990	**3.380**	**3.138**	2.364	2.820	**3.300**	23.464	3.487	2.430	3.234	3.656	3.394	2.557	3.050	3.569	25.377
6BBL[8]	1.68	**2.849**	2.590	**2.964**	2.767	2.646	2.364	2.706	2.657	21.544	3.082	2.801	3.206	2.993	2.862	2.557	2.926	2.874	23.301
		2.569	2.725	**2.894**	2.641	2.591	2.336	**2.839**	2.648	21.243	2.779	2.948	3.130	2.856	2.802	2.527	3.070	2.864	22.975
6OP1[9]	1.70	**3.173**	2.811	3.077	2.834	2.256	2.089	2.177	2.291	20.708	3.096	2.857	3.309	3.407	2.371	2.269	2.401	2.479	22.189
		2.862	2.642	3.060	**3.150**	2.192	2.098	2.220	2.292	20.516	3.432	3.040	3.327	3.065	2.440	2.259	2.354	2.478	22.396
6OP2[9]	1.9	3.020	2.886	**3.691**	**3.733**	2.226	1.901	2.157	2.248	21.862	4.319	3.499	4.086	3.779	2.534	2.151	2.386	2.512	25.266
		3.994	**3.235**	**3.778**	**3.494**	2.343	1.989	2.206	2.323	23.362	3.266	3.121	3.992	4.038	2.407	2.055	2.333	2.432	23.644
6OP4[9]	2.3	**3.216**	3.067	**3.905**	**3.780**	2.189	1.994	2.386	2.637	23.175	3.479	3.317	4.223	4.088	2.368	2.157	2.581	2.852	25.065
		7.873	**3.609**	**3.852**	**3.923**	2.543	1.940	2.191	2.478	**28.410**	8.515	3.904	4.166	4.243	2.751	2.098	2.369	2.680	30.726

Table S4 The abandoned bond valence analyses for irons in P-cluster [1] from MoFe protein 1MIO whose core structure modelled as [Fe_8S_8] at resolution of 3.0 Å. Bold bond distances and blank items present the valence of irons which are improper to be calculated due to unreasonable structures.

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–S1A	2.244	2.12	0.37	0.715			2.149	0.370	0.774		
Fe1–S1B	**4.538**	2.12	0.37				2.149	0.370			
Fe1–S2A	2.316	2.12	0.37	0.589			2.149	0.370	0.637		
Fe1–S3A	2.318	2.12	0.37	0.586			2.149	0.370	0.633		
Fe1–SG	2.307	2.12	0.37	0.603	Blank		2.149	0.370	0.652	Blank	
Fe2–S1A	2.317	2.12	0.37	0.587			2.149	0.370	0.635		
Fe2–S1B	**3.641**	2.12	0.37				2.149	0.370			
Fe2–S2A	2.272	2.12	0.37	0.663			2.149	0.370	0.717		
Fe2–S4A	2.332	2.12	0.37	0.564			2.149	0.370	0.610		
Fe2–SG	2.265	2.12	0.37	0.676	Blank		2.149	0.370	0.731	Blank	
Fe3–S2A	2.286	2.12	0.37	0.638			2.149	0.370	0.691		
Fe3–S3A	2.312	2.12	0.37	0.595			2.149	0.370	0.644		
Fe3–S4A	2.349	2.12	0.37	0.539			2.149	0.370	0.582		
Fe3–SG	2.279	2.12	0.37	0.651	2.423	0.423	2.149	0.370	0.704	2.620	-0.380

Fe4–S1A	2.302	2.12	0.37	0.611		2.149	0.370	0.661	
Fe4–S1B	**3.572**	2.12	0.37	0.020		2.149	0.370	0.021	
Fe4–S3A	2.312	2.12	0.37	0.595		2.149	0.370	0.644	
Fe4–S4A	2.301	2.12	0.37	0.613		2.149	0.370	0.663	
Fe4–SG	2.316	2.12	0.37	0.589	Blank	2.149	0.370	0.637	Blank
Fe5–S1A	**3.802**	2.12	0.37			2.149	0.370		
Fe5–S1B	2.309	2.12	0.37	0.600		2.149	0.370	0.649	
Fe5–S2B	2.302	2.12	0.37	0.611		2.149	0.370	0.661	
Fe5–S4B	2.330	2.12	0.37	0.567		2.149	0.370	0.613	
Fe5–SG	2.292	2.12	0.37	0.628		2.149	0.370	0.679	
Fe5–N	**2.949**	1.769	0.37		Blank	1.815	0.370		Blank
Fe6–S1A	**4.517**	2.12	0.37			2.149	0.370		
Fe6–S1B	2.246	2.12	0.37	0.711		2.149	0.370	0.769	
Fe6–S2B	2.294	2.12	0.37	0.625		2.149	0.370	0.676	
Fe6–S3B	2.316	2.12	0.37	0.589		2.149	0.370	0.637	
Fe6–SG	2.331	2.12	0.37	0.565		2.149	0.370	0.611	
Fe6–OG	2.218	1.715	0.37	0.257	Blank	1.749	0.370	0.282	Blank
Fe7–S2B	2.329	2.12	0.37	0.568		2.149	0.370	0.615	
Fe7–S3B	2.316	2.12	0.37	0.589		2.149	0.370	0.637	

Fe7–S4B	2.351	2.12	0.37	0.536			2.149	0.370	0.579		
Fe7–SG	2.322	2.12	0.37	0.579	2.272	0.272	2.149	0.370	0.627	2.457	-0.543
Fe8–S1A	**3.511**	2.12	0.37				2.149	0.370			
Fe8–S1B	2.314	2.12	0.37	0.592			2.149	0.370	0.640		
Fe8–S3B	2.276	2.12	0.37	0.656			2.149	0.370	0.709		
Fe8–S4B	2.340	2.12	0.37	0.552			2.149	0.370	0.597		
Fe8–SG	2.293	2.12	0.37	0.627	Blank		2.149	0.370	0.678	Blank	
					Blank					Blank	

Table S5 The abandoned bond valence analyses for irons in P-cluster [2] from MoFe protein 1MIO whose core structure modelled as [Fe_8S_8] at resolution of 3.0 Å. Bold bond distances and blank items present the valence of irons which are improper to be calculated due to unreasonable structures.

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–S1A	2.249	2.120	0.370	0.706			2.149	0.370	0.763		
Fe1–S1B	**4.570**	2.120	0.370				2.149	0.370			
Fe1–S2A	2.302	2.120	0.370	0.611			2.149	0.370	0.661		
Fe1–S3A	2.331	2.120	0.370	0.565			2.149	0.370	0.611		
Fe1–SG	2.305	2.120	0.370	0.607	Blank		2.149	0.370	0.656	Blank	
Fe2–S1A	2.284	2.120	0.370	0.642			2.149	0.370	0.694		

Fe2–S1B	**3.888**	2.120	0.370				2.149	0.370			
Fe2–S2A	2.265	2.120	0.370	0.676			2.149	0.370	0.731		
Fe2–S4A	2.304	2.120	0.370	0.608			2.149	0.370	0.658		
Fe2–SG	2.264	2.120	0.370	0.678	Blank		2.149	0.370	0.733	Blank	
Fe3–S2A	2.300	2.120	0.370	0.615			2.149	0.370	0.665		
Fe3–S3A	2.312	2.120	0.370	0.595			2.149	0.370	0.644		
Fe3–S4A	2.327	2.120	0.370	0.572			2.149	0.370	0.618		
Fe3–SG	2.302	2.120	0.370	0.611	2.393	0.393	2.149	0.370	0.661	2.588	-0.412
Fe4–S1A	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe4–S1B	**3.649**	2.120	0.370				2.149	0.370			
Fe4–S3A	2.310	2.120	0.370	0.598			2.149	0.370	0.647		
Fe4–S4A	2.321	2.120	0.370	0.581			2.149	0.370	0.628		
Fe4–SG	2.312	2.120	0.370	0.595	Blank		2.149	0.370	0.644	Blank	
Fe5–S1A	**3.606**	2.120	0.370				2.149	0.370			
Fe5–S1B	2.371	2.120	0.370	0.507			2.149	0.370	0.549		
Fe5–S2B	2.296	2.120	0.370	0.621			2.149	0.370	0.672		
Fe5–S4B	2.346	2.120	0.370	0.543			2.149	0.370	0.587		
Fe5–SG	2.276	2.120	0.370	0.656			2.149	0.370	0.709		
Fe5–N	**3.303**	1.769	0.370		Blank		1.815	0.370		Blank	

Fe6–S1A	**4.591**	2.120	0.370				2.149	0.370			
Fe6–S1B	2.293	2.120	0.370	0.627			2.149	0.370	0.678		
Fe6–S2B	2.297	2.120	0.370	0.620			2.149	0.370	0.670		
Fe6–S3B	2.303	2.120	0.370	0.610			2.149	0.370	0.660		
Fe6–SG	2.310	2.120	0.370	0.598			2.149	0.370	0.647		
Fe6–OG	2.211	1.715	0.370	0.262	Blank		1.749	0.370	0.287	Blank	
Fe7–S2B	2.330	2.120	0.370	0.567			2.149	0.370	0.613		
Fe7–S3B	2.336	2.120	0.370	0.558			2.149	0.370	0.603		
Fe7–S4B	2.312	2.120	0.370	0.595			2.149	0.370	0.644		
Fe7–SG	2.318	2.120	0.370	0.586	2.305	0.305	2.149	0.370	0.633	2.493	-0.507
Fe8–S1A	**3.249**	2.120	0.370				2.149	0.370			
Fe8–S1B	2.314	2.120	0.370	0.592			2.149	0.370	0.640		
Fe8–S3B	2.271	2.120	0.370	0.665			2.149	0.370	0.719		
Fe8–S4B	2.391	2.120	0.370	0.481			2.149	0.370	0.520		
Fe8–SG	2.258	2.120	0.370	0.689	Blank		2.149	0.370	0.745	Blank	
					Blank					Blank	

Table S6 The abandoned valence analyses for irons in P-cluster [1] from MoFe protein 3K1A which perform as P^N but its Fe3 and Fe7 dissociate with S atom at resolution of 2.3 Å. Bold bond distances and blank items present the valence of irons which are improper to be calculated due to unreasonable structures.

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	2.579	2.12	0.37	0.289			2.149	0.37	0.313		
Fe1–S2A	2.249	2.12	0.37	0.706			2.149	0.37	0.763		
Fe1–S3A	2.189	2.12	0.37	0.830			2.149	0.37	0.898		
Fe1–SG	2.442	2.12	0.37	0.419	2.244	0.244	2.149	0.37	0.453	2.426	-0.574
Fe2–S1	1.928	2.12	0.37	1.680			2.149	0.37	1.817		
Fe2–S2A	2.192	2.12	0.37	0.823			2.149	0.37	0.890		
Fe2–S4A	2.230	2.12	0.37	0.743			2.149	0.37	0.803		
Fe2–SG	2.624	2.12	0.37	0.256	**3.502**	1.502	2.149	0.37	0.277	3.788	0.788
Fe3–S2A	2.175	2.12	0.37	0.862			2.149	0.37	0.932		
Fe3–S3A	2.191	2.12	0.37	0.825			2.149	0.37	0.893		
Fe3–S4A	2.172	2.12	0.37	0.869			2.149	0.37	0.940		
Fe3–SG	**2.746**	2.12	0.37		Blank		2.149	0.37		Blank	
Fe4–S1	2.126	2.12	0.37	0.984			2.149	0.37	1.064		
Fe4–S3A	2.209	2.12	0.37	0.786			2.149	0.37	0.850		

Fe4–S4A	2.215	2.12	0.37	0.774			2.149	0.37	0.837		
Fe4–SG	2.198	2.12	0.37	0.810	**3.354**	1.354	2.149	0.37	0.876	3.627	0.627
Fe5–S1	2.160	2.12	0.37	0.898			2.149	0.37	0.971		
Fe5–S2B	2.223	2.12	0.37	0.757			2.149	0.37	0.819		
Fe5–S4B	2.218	2.12	0.37	0.767			2.149	0.37	0.830		
Fe5–SG	2.313	2.12	0.37	0.594	**3.015**	1.015	2.149	0.37	0.642	3.261	0.261
Fe6–S1	2.192	2.12	0.37	0.823			2.149	0.37	0.890		
Fe6–S2B	2.206	2.12	0.37	0.793			2.149	0.37	0.857		
Fe6–S3B	2.208	2.12	0.37	0.788			2.149	0.37	0.853		
Fe6–SG	2.698	2.12	0.37	0.210	2.614	0.614	2.149	0.37	0.227	2.827	-0.173
Fe7–S2B	2.203	2.12	0.37	0.799			2.149	0.37	0.864		
Fe7–S3B	2.169	2.12	0.37	0.876			2.149	0.37	0.947		
Fe7–S4B	2.152	2.12	0.37	0.917			2.149	0.37	0.992		
Fe7–SG	**3.281**	2.12	0.37		Blank		2.149	0.37		Blank	
Fe8–S1	1.961	2.12	0.37	1.537			2.149	0.37	1.662		
Fe8–S3B	2.234	2.12	0.37	0.735			2.149	0.37	0.795		
Fe8–S4B	2.236	2.12	0.37	0.731			2.149	0.37	0.790		
Fe8–SG	2.285	2.12	0.37	0.640	**3.643**	1.643	2.149	0.37	0.692	3.940	0.940
					Blank					Blank	

Table S7 The abandoned valence analyses for irons in P-cluster [2] from MoFe protein 3K1A which perform as P^N but its Fe3 and Fe7 dissociate with S atom at resolution of 2.3 Å. Bold bond distances and blank items present the valence of iron which are improper to be calculated due to unreasonable structures.

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	2.578	2.12	0.37	0.290			2.149	0.37	0.314		
Fe1–S2A	2.240	2.12	0.37	0.723			2.149	0.37	0.782		
Fe1–S3A	2.208	2.12	0.37	0.788			2.149	0.37	0.853		
Fe1–SG	2.377	2.12	0.37	0.499	2.301	0.301	2.149	0.37	0.540	2.488	-0.512
Fe2–S1	1.907	2.12	0.37	1.778			2.149	0.37	1.923		
Fe2–S2A	2.197	2.12	0.37	0.812			2.149	0.37	0.878		
Fe2–S4A	2.228	2.12	0.37	0.747			2.149	0.37	0.808		
Fe2–SG	2.596	2.12	0.37	0.276	**3.614**	1.614	2.149	0.37	0.299	3.908	0.908
Fe3–S2A	2.174	2.12	0.37	0.864			2.149	0.37	0.935		
Fe3–S3A	2.175	2.12	0.37	0.862			2.149	0.37	0.932		
Fe3–S4A	2.173	2.12	0.37	0.867			2.149	0.37	0.937		
Fe3–SG	**2.734**	2.12	0.37		Blank		2.149	0.37		Blank	
Fe4–S1	2.114	2.12	0.37	1.016			2.149	0.37	1.099		
Fe4–S3A	2.212	2.12	0.37	0.780			2.149	0.37	0.843		

Fe4–S4A	2.213	2.12	0.37	0.778			2.149	0.37	0.841		
Fe4–SG	2.261	2.12	0.37	0.683	**3.257**	1.257	2.149	0.37	0.739	3.523	0.523
Fe5–S1	2.132	2.12	0.37	0.968			2.149	0.37	1.047		
Fe5–S2B	2.227	2.12	0.37	0.749			2.149	0.37	0.810		
Fe5–S4B	2.200	2.12	0.37	0.806			2.149	0.37	0.871		
Fe5–SG	2.231	2.12	0.37	0.741	**3.263**	1.263	2.149	0.37	0.801	3.529	0.529
Fe6–S1	2.174	2.12	0.37	0.864			2.149	0.37	0.935		
Fe6–S2B	2.193	2.12	0.37	0.821			2.149	0.37	0.888		
Fe6–S3B	2.204	2.12	0.37	0.797			2.149	0.37	0.862		
Fe6–SG	2.549	2.12	0.37	0.314	2.796	0.796	2.149	0.37	0.339	3.024	0.024
Fe7–S2B	2.211	2.12	0.37	0.782			2.149	0.37	0.846		
Fe7–S3B	2.162	2.12	0.37	0.893			2.149	0.37	0.965		
Fe7–S4B	2.162	2.12	0.37	0.893			2.149	0.37	0.965		
Fe7–SG	**3.265**	2.12	0.37		Blank		2.149	0.37		Blank	
Fe8–S1	1.982	2.12	0.37	1.452			2.149	0.37	1.570		
Fe8–S3B	2.240	2.12	0.37	0.723			2.149	0.37	0.782		
Fe8–S4B	2.222	2.12	0.37	0.759			2.149	0.37	0.821		
Fe8–SG	2.266	2.12	0.37	0.674	**3.608**	1.608	2.149	0.37	0.729	3.902	0.902
					Blank					Blank	

Table S8 The abandoned valence analyses for irons in P-cluster [1] from MoFe protein 6O7S which absent Fe1 and Fe5 at resolution of 2.7Å. Blank items present the valence of irons which are improper to be calculated due to unreasonable structures.

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											
Fe1–S2A											
Fe1–S3A											
Fe1–SG					Blank					Blank	
Fe2–S1	2.372	2.12	0.37	0.506			2.149	0.37	0.547		
Fe2–S2A	2.261	2.12	0.37	0.683			2.149	0.37	0.739		
Fe2–S4A	2.274	2.12	0.37	0.660			2.149	0.37	0.713		
Fe2–SG	2.372	2.12	0.37	0.506	2.355	0.355	2.149	0.37	0.547	2.547	-0.453
Fe3–S2A	2.270	2.12	0.37	0.667			2.149	0.37	0.721		
Fe3–S3A	2.253	2.12	0.37	0.698			2.149	0.37	0.755		
Fe3–S4A	2.298	2.12	0.37	0.618			2.149	0.37	0.669		
Fe3–SG	2.299	2.12	0.37	0.616	2.599	0.599	2.149	0.37	0.667	2.811	-0.189
Fe4–S1	2.330	2.12	0.37	0.567			2.149	0.37	0.613		
Fe4–S3A	2.269	2.12	0.37	0.669			2.149	0.37	0.723		

Fe4–S4A	2.285	2.12	0.37	0.640			2.149	0.37	0.692		
Fe4–SG	2.382	2.12	0.37	0.493	2.368	0.368	2.149	0.37	0.533	2.561	-0.439
Fe5–S1											
Fe5–S2B											
Fe5–S4B											
Fe5–SG					Blank					Blank	
Fe6–S1	2.612	2.12	0.37	0.265			2.149	0.37	0.286		
Fe6–S2B	2.315	2.12	0.37	0.590			2.149	0.37	0.638		
Fe6–S3B	2.309	2.12	0.37	0.600			2.149	0.37	0.649		
Fe6–SG	2.406	2.12	0.37	0.462	1.917	-0.083	2.149	0.37	0.499	2.073	-0.927
Fe7–S2B	2.294	2.12	0.37	0.625			2.149	0.37	0.676		
Fe7–S3B	2.296	2.12	0.37	0.621			2.149	0.37	0.672		
Fe7–S4B	2.277	2.12	0.37	0.654			2.149	0.37	0.708		
Fe7–SG	2.400	2.12	0.37	0.469	2.370	0.370	2.149	0.37	0.507	2.563	-0.437
Fe8–S1	2.307	2.12	0.37	0.603			2.149	0.37	0.652		
Fe8–S3B	2.305	2.12	0.37	0.607			2.149	0.37	0.656		
Fe8–S4B	2.317	2.12	0.37	0.587			2.149	0.37	0.635		
Fe8–SG	2.283	2.12	0.37	0.644	2.441	0.441	2.149	0.37	0.696	2.640	-0.360
					Blank					Blank	

Table S9 The abandoned valence analyses for irons in P-cluster [2] from MoFe protein 6O7S which absent Fe1 and Fe5 at resolution of 2.7 Å. Blank items present the valence of irons which are improper to be calculated due to unreasonable structures.

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											
Fe1–S2A											
Fe1–S3A											
Fe1–SG					Blank					Blank	
Fe2–S1	2.374	2.120	0.370	0.503			2.149	0.370	0.544		
Fe2–S2A	2.246	2.120	0.370	0.711			2.149	0.370	0.769		
Fe2–S4A	2.297	2.120	0.370	0.620			2.149	0.370	0.670		
Fe2–SG	2.432	2.120	0.370	0.430	2.265	0.265	2.149	0.370	0.465	2.449	-0.551
Fe3–S2A	2.283	2.120	0.370	0.644			2.149	0.370	0.696		
Fe3–S3A	2.244	2.120	0.370	0.715			2.149	0.370	0.774		
Fe3–S4A	2.301	2.120	0.370	0.613			2.149	0.370	0.663		
Fe3–SG	2.316	2.120	0.370	0.589	2.561	0.561	2.149	0.370	0.637	2.770	-0.230
Fe4–S1	2.336	2.120	0.370	0.558			2.149	0.370	0.603		
Fe4–S3A	2.265	2.120	0.370	0.676			2.149	0.370	0.731		

Fe4–S4A	2.283	2.120	0.370	0.644			2.149	0.370	0.696		
Fe4–SG	2.354	2.120	0.370	0.531	2.409	0.409	2.149	0.370	0.575	2.605	-0.395
Fe5–S1											
Fe5–S2B											
Fe5–S4B											
Fe5–SG					Blank					Blank	
Fe6–S1	2.622	2.120	0.370	0.257			2.149	0.370	0.278		
Fe6–S2B	2.313	2.120	0.370	0.594			2.149	0.370	0.642		
Fe6–S3B	2.303	2.120	0.370	0.610			2.149	0.370	0.660		
Fe6–SG	2.405	2.120	0.370	0.463	1.924	-0.076	2.149	0.370	0.501	2.081	-0.919
Fe7–S2B	2.310	2.120	0.370	0.598			2.149	0.370	0.647		
Fe7–S3B	2.306	2.120	0.370	0.605			2.149	0.370	0.654		
Fe7–S4B	2.280	2.120	0.370	0.649			2.149	0.370	0.702		
Fe7–SG	2.420	2.120	0.370	0.444	2.297	0.297	2.149	0.370	0.481	2.484	-0.516
Fe8–S1	2.289	2.120	0.370	0.633			2.149	0.370	0.685		
Fe8–S3B	2.306	2.120	0.370	0.605			2.149	0.370	0.654		
Fe8–S4B	2.319	2.120	0.370	0.584			2.149	0.370	0.632		
Fe8–SG	2.269	2.120	0.370	0.669	2.491	0.491	2.149	0.370	0.723	2.694	-0.306
					Blank					Blank	

Table S10 The abandoned valence analyses for irons in P-cluster [1] from MoFe protein 1M1Y at resolution of 3.2 Å. Faulty data in R_0 (+2) are bold highlighted.

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	2.508	2.120	0.370	0.350			2.149	0.370	0.379		
Fe1–S2A	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe1–S3A	2.266	2.120	0.370	0.674			2.149	0.370	0.729		
Fe1–SG	2.213	2.120	0.370	0.778	2.444	0.444	2.149	0.370	0.841	2.643	-0.357
Fe2–S1	2.331	2.120	0.370	0.565			2.149	0.370	0.611		
Fe2–S2A	2.157	2.120	0.370	0.905			2.149	0.370	0.979		
Fe2–S4A	2.205	2.120	0.370	0.795			2.149	0.370	0.860		
Fe2–SG	2.670	2.120	0.370	0.226	2.491	0.491	2.149	0.370	0.245	2.694	-0.306
Fe3–S2A	2.306	2.120	0.370	0.605			2.149	0.370	0.654		
Fe3–S3A	2.260	2.120	0.370	0.685			2.149	0.370	0.741		
Fe3–S4A	2.247	2.120	0.370	0.709			2.149	0.370	0.767		
Fe3–SG	1.980	2.120	0.370	1.460	**3.459**	1.459	2.149	0.370	1.579	3.741	0.741
Fe4–S1	2.558	2.120	0.370	0.306			2.149	0.370	0.331		
Fe4–S3A	2.217	2.120	0.370	0.769			2.149	0.370	0.832		
Fe4–S4A	2.241	2.120	0.370	0.721			2.149	0.370	0.780		

Fe4–SG	1.717	2.120	0.370	2.972	**4.768**	2.768	2.149	0.370	3.214	5.157	2.157
Fe5–S1	2.579	2.120	0.370	0.289			2.149	0.370	0.313		
Fe5–S2B	2.312	2.120	0.370	0.595			2.149	0.370	0.644		
Fe5–S4B	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe5–SG	1.822	2.120	0.370	2.238	**3.762**	1.762	2.149	0.370	2.420	4.069	1.069
Fe6–S1	2.369	2.120	0.370	0.510			2.149	0.370	0.552		
Fe6–S2B	2.200	2.120	0.370	0.806			2.149	0.370	0.871		
Fe6–S3B	2.239	2.120	0.370	0.725			2.149	0.370	0.784		
Fe6–SG	2.807	2.120	0.370	0.156	2.197	0.197	2.149	0.370	0.169	2.376	-0.624
Fe7–S2B	2.353	2.120	0.370	0.533			2.149	0.370	0.576		
Fe7–S3B	2.358	2.120	0.370	0.526			2.149	0.370	0.568		
Fe7–S4B	2.291	2.120	0.370	0.630			2.149	0.370	0.681		
Fe7–SG	2.600	2.120	0.370	0.273	1.962	-0.038	2.149	0.370	0.296	2.121	-0.879
Fe8–S1	2.519	2.120	0.370	0.340			2.149	0.370	0.368		
Fe8–S3B	2.303	2.120	0.370	0.610			2.149	0.370	0.660		
Fe8–S4B	2.389	2.120	0.370	0.483			2.149	0.370	0.523		
Fe8–SG	1.903	2.120	0.370	1.798	**3.231**	1.231	2.149	0.370	1.944	3.494	0.494
					24.314					26.297	

Table S11 The abandoned valence analyses for irons in P-cluster [2] from MoFe protein 1M1Y at resolution of 3.2 Å. Faulty data in R_0 (+2) are bold highlighted.

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	2.530	2.120	0.370	0.330			2.149	0.370	0.357		
Fe1–S2A	2.271	2.120	0.370	0.665			2.149	0.370	0.719		
Fe1–S3A	2.276	2.120	0.370	0.656			2.149	0.370	0.709		
Fe1–SG	2.097	2.120	0.370	1.064	2.715	0.715	2.149	0.370	1.151	2.937	-0.063
Fe2–S1	2.268	2.120	0.370	0.670			2.149	0.370	0.725		
Fe2–S2A	2.192	2.120	0.370	0.823			2.149	0.370	0.890		
Fe2–S4A	2.244	2.120	0.370	0.715			2.149	0.370	0.774		
Fe2–SG	2.839	2.120	0.370	0.143	2.352	0.352	2.149	0.370	0.155	2.544	-0.456
Fe3–S2A	2.330	2.120	0.370	0.567			2.149	0.370	0.613		
Fe3–S3A	2.296	2.120	0.370	0.621			2.149	0.370	0.672		
Fe3–S4A	2.259	2.120	0.370	0.687			2.149	0.370	0.743		
Fe3–SG	2.068	2.120	0.370	1.151	3.026	1.026	2.149	0.370	1.245	3.273	0.273
Fe4–S1	2.515	2.120	0.370	0.344			2.149	0.370	0.372		
Fe4–S3A	2.309	2.120	0.370	0.600			2.149	0.370	0.649		

Fe4–S4A	2.238	2.120	0.370	0.727			2.149	0.370	0.786		
Fe4–SG	1.837	2.120	0.370	2.149	**3.819**	1.819	2.149	0.370	2.324	4.131	1.131
Fe5–S1	2.570	2.120	0.370	0.296			2.149	0.370	0.321		
Fe5–S2B	2.257	2.120	0.370	0.691			2.149	0.370	0.747		
Fe5–S4B	2.303	2.120	0.370	0.610			2.149	0.370	0.660		
Fe5–SG	1.929	2.120	0.370	1.676	**3.272**	1.272	2.149	0.370	1.812	3.539	0.539
Fe6–S1	2.355	2.120	0.370	0.530			2.149	0.370	0.573		
Fe6–S2B	2.224	2.120	0.370	0.755			2.149	0.370	0.817		
Fe6–S3B	2.168	2.120	0.370	0.878			2.149	0.370	0.950		
Fe6–SG	2.858	2.120	0.370	0.136	2.299	0.299	2.149	0.370	0.147	2.487	-0.513
Fe7–S2B	2.312	2.120	0.370	0.595			2.149	0.370	0.644		
Fe7–S3B	2.313	2.120	0.370	0.594			2.149	0.370	0.642		
Fe7–S4B	2.275	2.120	0.370	0.658			2.149	0.370	0.711		
Fe7–SG	2.744	2.120	0.370	0.185	2.032	0.032	2.149	0.370	0.200	2.197	-0.803
Fe8–S1	2.523	2.120	0.370	0.336			2.149	0.370	0.364		
Fe8–S3B	2.251	2.120	0.370	0.702			2.149	0.370	0.759		
Fe8–S4B	2.311	2.120	0.370	0.597			2.149	0.370	0.645		
Fe8–SG	1.894	2.120	0.370	1.842	**3.477**	1.477	2.149	0.370	1.992	3.761	0.761
					22.993					24.868	

Table S12 The abandoned valence analyses for irons in P-cluster [3] from MoFe protein 1M1Y at resolution of 3.2 Å. Faulty data in R_0 (+2) are bold highlighted.

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	2.470	2.120	0.370	0.388			2.149	0.370	0.420		
Fe1–S2A	2.258	2.120	0.370	0.689			2.149	0.370	0.745		
Fe1–S3A	2.329	2.120	0.370	0.568			2.149	0.370	0.615		
Fe1–SG	1.987	2.120	0.370	1.433	3.078	1.078	2.149	0.370	1.549	3.329	0.329
Fe2–S1	2.307	2.120	0.370	0.603			2.149	0.370	0.652		
Fe2–S2A	2.152	2.120	0.370	0.917			2.149	0.370	0.992		
Fe2–S4A	2.158	2.120	0.370	0.902			2.149	0.370	0.976		
Fe2–SG	2.856	2.120	0.370	0.137	2.560	0.560	2.149	0.370	0.148	2.768	-0.232
Fe3–S2A	2.281	2.120	0.370	0.647			2.149	0.370	0.700		
Fe3–S3A	2.211	2.120	0.370	0.782			2.149	0.370	0.846		
Fe3–S4A	2.228	2.120	0.370	0.747			2.149	0.370	0.808		
Fe3–SG	2.150	2.120	0.370	0.922	3.098	1.098	2.149	0.370	0.997	3.351	0.351
Fe4–S1	2.454	2.120	0.370	0.405			2.149	0.370	0.439		
Fe4–S3A	2.221	2.120	0.370	0.761			2.149	0.370	0.823		

Fe4–S4A	2.264	2.120	0.370	0.678			2.149	0.370	0.733		
Fe4–SG	1.635	2.120	0.370	3.709	5.553	3.553	2.149	0.370	4.012	6.006	3.006
Fe5–S1	2.549	2.120	0.370	0.314			2.149	0.370	0.339		
Fe5–S2B	2.267	2.120	0.370	0.672			2.149	0.370	0.727		
Fe5–S4B	2.317	2.120	0.370	0.587			2.149	0.370	0.635		
Fe5–SG	1.727	2.120	0.370	2.893	4.466	2.466	2.149	0.370	3.128	4.830	1.830
Fe6–S1	2.338	2.120	0.370	0.555			2.149	0.370	0.600		
Fe6–S2B	2.200	2.120	0.370	0.806			2.149	0.370	0.871		
Fe6–S3B	2.176	2.120	0.370	0.860			2.149	0.370	0.930		
Fe6–SG	2.613	2.120	0.370	0.264	2.484	0.484	2.149	0.370	0.285	2.686	-0.314
Fe7–S2B	2.244	2.120	0.370	0.715			2.149	0.370	0.774		
Fe7–S3B	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe7–S4B	2.268	2.120	0.370	0.670			2.149	0.370	0.725		
Fe7–SG	2.483	2.120	0.370	0.375	2.401	0.401	2.149	0.370	0.405	2.596	-0.404
Fe8–S1	2.462	2.120	0.370	0.397			2.149	0.370	0.429		
Fe8–S3B	2.267	2.120	0.370	0.672			2.149	0.370	0.727		
Fe8–S4B	2.349	2.120	0.370	0.539			2.149	0.370	0.582		
Fe8–SG	1.906	2.120	0.370	1.783	3.391	1.391	2.149	0.370	1.929	3.667	0.667
					27.030					29.233	

Table S13 The abandoned valence analyses for irons in P-cluster [4] from MoFe protein 1M1Y at resolution of 3.2 Å. Faulty data in R_0 (+2) are bold highlighted.

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	2.490	2.120	0.370	0.368			2.149	0.370	0.398		
Fe1–S2A	2.260	2.120	0.370	0.685			2.149	0.370	0.741		
Fe1–S3A	2.218	2.120	0.370	0.767			2.149	0.370	0.830		
Fe1–SG	2.030	2.120	0.370	1.275	3.096	1.096	2.149	0.370	1.379	3.348	0.348
Fe2–S1	2.279	2.120	0.370	0.651			2.149	0.370	0.704		
Fe2–S2A	2.167	2.120	0.370	0.881			2.149	0.370	0.953		
Fe2–S4A	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe2–SG	2.868	2.120	0.370	0.132	2.316	0.316	2.149	0.370	0.143	2.505	-0.495
Fe3–S2A	2.370	2.120	0.370	0.509			2.149	0.370	0.550		
Fe3–S3A	2.304	2.120	0.370	0.608			2.149	0.370	0.658		
Fe3–S4A	2.258	2.120	0.370	0.689			2.149	0.370	0.745		
Fe3–SG	2.134	2.120	0.370	0.963	2.769	0.769	2.149	0.370	1.041	2.994	-0.006
Fe4–S1	2.456	2.120	0.370	0.403			2.149	0.370	0.436		
Fe4–S3A	2.333	2.120	0.370	0.562			2.149	0.370	0.608		

Fe4–S4A	2.323	2.120	0.370	0.578			2.149	0.370	0.625		
Fe4–SG	1.906	2.120	0.370	1.783	**3.326**	1.326	2.149	0.370	1.929	3.598	0.598
Fe5–S1	2.543	2.120	0.370	0.319			2.149	0.370	0.345		
Fe5–S2B	2.266	2.120	0.370	0.674			2.149	0.370	0.729		
Fe5–S4B	2.316	2.120	0.370	0.589			2.149	0.370	0.637		
Fe5–SG	1.943	2.120	0.370	1.613	**3.195**	1.195	2.149	0.370	1.745	3.455	0.455
Fe6–S1	2.289	2.120	0.370	0.633			2.149	0.370	0.685		
Fe6–S2B	2.230	2.120	0.370	0.743			2.149	0.370	0.803		
Fe6–S3B	2.236	2.120	0.370	0.731			2.149	0.370	0.790		
Fe6–SG	2.705	2.120	0.370	0.206	2.313	0.313	2.149	0.370	0.223	2.501	-0.499
Fe7–S2B	2.312	2.120	0.370	0.595			2.149	0.370	0.644		
Fe7–S3B	2.351	2.120	0.370	0.536			2.149	0.370	0.579		
Fe7–S4B	2.326	2.120	0.370	0.573			2.149	0.370	0.620		
Fe7–SG	2.579	2.120	0.370	0.289	1.993	-0.007	2.149	0.370	0.313	2.156	-0.844
Fe8–S1	2.458	2.120	0.370	0.401			2.149	0.370	0.434		
Fe8–S3B	2.293	2.120	0.370	0.627			2.149	0.370	0.678		
Fe8–S4B	2.331	2.120	0.370	0.565			2.149	0.370	0.611		
Fe8–SG	2.043	2.120	0.370	1.231	2.824	0.824	2.149	0.370	1.332	3.055	0.055
					21.832					23.612	

Table S14 The abandoned valence analyses for irons in P-cluster [1] from MoFe protein 2AFI at resolution of 3.1 Å. Faulty data in R_0 (+2) are bold highlighted.

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	2.227	2.12	0.37	0.749			2.149	0.37	0.810		
Fe1–S2A	2.215	2.12	0.37	0.774			2.149	0.37	0.837		
Fe1–S3A	2.234	2.12	0.37	0.735			2.149	0.37	0.795		
Fe1–SG	2.248	2.12	0.37	0.708	2.965	0.965	2.149	0.37	0.765	3.207	0.207
Fe2–S1	2.495	2.12	0.37	0.363			2.149	0.37	0.393		
Fe2–S2A	2.281	2.12	0.37	0.647			2.149	0.37	0.700		
Fe2–S4A	2.251	2.12	0.37	0.702			2.149	0.37	0.759		
Fe2–SG	2.305	2.12	0.37	0.607	2.318	0.318	2.149	0.37	0.656	2.508	-0.492
Fe3–S2A	2.195	2.12	0.37	0.817			2.149	0.37	0.883		
Fe3–S3A	2.221	2.12	0.37	0.761			2.149	0.37	0.823		
Fe3–S4A	2.240	2.12	0.37	0.723			2.149	0.37	0.782		
Fe3–SG	2.271	2.12	0.37	0.665	2.966	0.966	2.149	0.37	0.719	3.207	0.207
Fe4–S1	2.071	2.12	0.37	1.142			2.149	0.37	1.235		
Fe4–S3A	2.226	2.12	0.37	0.751			2.149	0.37	0.812		

Fe4–S4A	2.199	2.12	0.37	0.808			2.149	0.37	0.874		
Fe4–SG	2.198	2.12	0.37	0.810	**3.510**	1.510	2.149	0.37	0.876	3.796	0.796
Fe5–S1	2.079	2.12	0.37	1.117			2.149	0.37	1.208		
Fe5–S2B	2.221	2.12	0.37	0.761			2.149	0.37	0.823		
Fe5–S4B	2.257	2.12	0.37	0.691			2.149	0.37	0.747		
Fe5–SG	2.276	2.12	0.37	0.656	**3.225**	1.225	2.149	0.37	0.709	3.488	0.488
Fe6–S1	2.480	2.12	0.37	0.378			2.149	0.37	0.409		
Fe6–S2B	2.300	2.12	0.37	0.615			2.149	0.37	0.665		
Fe6–S3B	2.257	2.12	0.37	0.691			2.149	0.37	0.747		
Fe6–SG	2.226	2.12	0.37	0.751	2.434	0.434	2.149	0.37	0.812	2.633	-0.367
Fe7–S2B	2.262	2.12	0.37	0.681			2.149	0.37	0.737		
Fe7–S3B	2.223	2.12	0.37	0.757			2.149	0.37	0.819		
Fe7–S4B	2.244	2.12	0.37	0.715			2.149	0.37	0.774		
Fe7–SG	2.306	2.12	0.37	0.605	2.758	0.758	2.149	0.37	0.654	2.983	-0.017
Fe8–S1	2.202	2.12	0.37	0.801			2.149	0.37	0.867		
Fe8–S3B	2.202	2.12	0.37	0.801			2.149	0.37	0.867		
Fe8–S4B	2.226	2.12	0.37	0.751			2.149	0.37	0.812		
Fe8–SG	2.143	2.12	0.37	0.940	**3.293**	1.293	2.149	0.37	1.016	3.562	0.562
					23.470					25.383	

Table S15 The abandoned valence analyses for irons in P-cluster [2] from MoFe protein 2AFI at resolution of 3.1 Å. Faulty data in R_0 (+2) are bold highlighted.

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	2.228	2.12	0.37	0.747			2.149	0.37	0.808		
Fe1–S2A	2.197	2.12	0.37	0.812			2.149	0.37	0.878		
Fe1–S3A	2.221	2.12	0.37	0.761			2.149	0.37	0.823		
Fe1–SG	2.245	2.12	0.37	0.713	3.033	1.033	2.149	0.37	0.771	3.281	0.281
Fe2–S1	2.527	2.12	0.37	0.333			2.149	0.37	0.360		
Fe2–S2A	2.264	2.12	0.37	0.678			2.149	0.37	0.733		
Fe2–S4A	2.263	2.12	0.37	0.679			2.149	0.37	0.735		
Fe2–SG	2.269	2.12	0.37	0.669	2.358	0.358	2.149	0.37	0.723	2.551	-0.449
Fe3–S2A	2.189	2.12	0.37	0.830			2.149	0.37	0.898		
Fe3–S3A	2.226	2.12	0.37	0.751			2.149	0.37	0.812		
Fe3–S4A	2.216	2.12	0.37	0.771			2.149	0.37	0.834		
Fe3–SG	2.279	2.12	0.37	0.651	3.003	1.003	2.149	0.37	0.704	3.248	0.248
Fe4–S1	2.120	2.12	0.37	1.000			2.149	0.37	1.082		
Fe4–S3A	2.249	2.12	0.37	0.706			2.149	0.37	0.763		

Fe4–S4A	2.197	2.12	0.37	0.812			2.149	0.37	0.878		
Fe4–SG	2.195	2.12	0.37	0.817	**3.334**	1.334	2.149	0.37	0.883	3.606	0.606
Fe5–S1	2.099	2.12	0.37	1.058			2.149	0.37	1.145		
Fe5–S2B	2.229	2.12	0.37	0.745			2.149	0.37	0.806		
Fe5–S4B	2.239	2.12	0.37	0.725			2.149	0.37	0.784		
Fe5–SG	2.279	2.12	0.37	0.651	**3.179**	1.179	2.149	0.37	0.704	3.438	0.438
Fe6–S1	2.530	2.12	0.37	0.330			2.149	0.37	0.357		
Fe6–S2B	2.247	2.12	0.37	0.709			2.149	0.37	0.767		
Fe6–S3B	2.222	2.12	0.37	0.759			2.149	0.37	0.821		
Fe6–SG	2.262	2.12	0.37	0.681	2.480	0.480	2.149	0.37	0.737	2.682	-0.318
Fe7–S2B	2.232	2.12	0.37	0.739			2.149	0.37	0.799		
Fe7–S3B	2.207	2.12	0.37	0.790			2.149	0.37	0.855		
Fe7–S4B	2.251	2.12	0.37	0.702			2.149	0.37	0.759		
Fe7–SG	2.316	2.12	0.37	0.589	2.820	0.820	2.149	0.37	0.637	3.050	0.050
Fe8–S1	2.102	2.12	0.37	1.050			2.149	0.37	1.135		
Fe8–S3B	2.207	2.12	0.37	0.790			2.149	0.37	0.855		
Fe8–S4B	2.237	2.12	0.37	0.729			2.149	0.37	0.788		
Fe8–SG	2.224	2.12	0.37	0.755	**3.324**	1.324	2.149	0.37	0.817	3.595	0.595
					23.532					25.451	

Table S16 The abandoned valence analyses for irons in P-cluster [3] from MoFe protein 2AFI at resolution of 3.1 Å. Faulty data in R_0 (+2) are bold highlighted.

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	2.159	2.12	0.37	0.900			2.149	0.37	0.973		
Fe1–S2A	2.212	2.12	0.37	0.780			2.149	0.37	0.843		
Fe1–S3A	2.200	2.12	0.37	0.806			2.149	0.37	0.871		
Fe1–SG	2.157	2.12	0.37	0.905	**3.390**	1.390	2.149	0.37	0.979	3.667	0.667
Fe1–S1	2.504	2.12	0.37	0.354			2.149	0.37	0.383		
Fe1–S2A	2.227	2.12	0.37	0.749			2.149	0.37	0.810		
Fe1–S3A	2.244	2.12	0.37	0.715			2.149	0.37	0.774		
Fe1–SG	2.253	2.12	0.37	0.698	2.516	0.516	2.149	0.37	0.755	2.722	-0.278
Fe1–S1	2.234	2.12	0.37	0.735			2.149	0.37	0.795		
Fe1–S2A	2.217	2.12	0.37	0.769			2.149	0.37	0.832		
Fe1–S3A	2.201	2.12	0.37	0.803			2.149	0.37	0.869		
Fe1–SG	2.291	2.12	0.37	0.630	2.938	0.938	2.149	0.37	0.681	3.177	0.177
Fe1–S1	2.037	2.12	0.37	1.251			2.149	0.37	1.354		
Fe1–S2A	2.209	2.12	0.37	0.786			2.149	0.37	0.850		

Fe1–S3A	2.192	2.12	0.37	0.823			2.149	0.37	0.890		
Fe1–SG	2.173	2.12	0.37	0.867	**3.727**	1.727	2.149	0.37	0.937	4.031	1.031
Fe1–S1	2.098	2.12	0.37	1.061			2.149	0.37	1.148		
Fe1–S2A	2.201	2.12	0.37	0.803			2.149	0.37	0.869		
Fe1–S3A	2.294	2.12	0.37	0.625			2.149	0.37	0.676		
Fe1–SG	2.241	2.12	0.37	0.721	**3.211**	1.211	2.149	0.37	0.780	3.472	0.472
Fe1–S1	2.476	2.12	0.37	0.382			2.149	0.37	0.413		
Fe1–S2A	2.277	2.12	0.37	0.654			2.149	0.37	0.708		
Fe1–S3A	2.251	2.12	0.37	0.702			2.149	0.37	0.759		
Fe1–SG	2.223	2.12	0.37	0.757	2.495	0.495	2.149	0.37	0.819	2.699	-0.301
Fe1–S1	2.227	2.12	0.37	0.749			2.149	0.37	0.810		
Fe1–S2A	2.211	2.12	0.37	0.782			2.149	0.37	0.846		
Fe1–S3A	2.239	2.12	0.37	0.725			2.149	0.37	0.784		
Fe1–SG	2.326	2.12	0.37	0.573	2.829	0.829	2.149	0.37	0.620	3.060	0.060
Fe1–S1	2.153	2.12	0.37	0.915			2.149	0.37	0.989		
Fe1–S2A	2.190	2.12	0.37	0.828			2.149	0.37	0.895		
Fe1–S3A	2.233	2.12	0.37	0.737			2.149	0.37	0.797		
Fe1–SG	2.166	2.12	0.37	0.883	**3.362**	1.362	2.149	0.37	0.955	3.636	0.636
Fe1–S1					**24.468**					26.463	

Table S17 The abandoned valence analyses for irons in P-cluster [4] from MoFe protein 2AFI at resolution of 3.1 Å. Faulty data in R_0 (+2) are bold highlighted.

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	2.162	2.120	0.370	0.893			2.149	0.370	0.965		
Fe1–S2A	2.224	2.120	0.370	0.755			2.149	0.370	0.817		
Fe1–S3A	2.226	2.120	0.370	0.751			2.149	0.370	0.812		
Fe1–SG	2.191	2.120	0.370	0.825	**3.224**	1.224	2.149	0.370	0.893	3.487	0.487
Fe2–S1	2.510	2.120	0.370	0.349			2.149	0.370	0.377		
Fe2–S2A	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe2–S4A	2.293	2.120	0.370	0.627			2.149	0.370	0.678		
Fe2–SG	2.288	2.120	0.370	0.635	2.247	0.247	2.149	0.370	0.687	2.430	-0.570
Fe3–S2A	2.229	2.120	0.370	0.745			2.149	0.370	0.806		
Fe3–S3A	2.188	2.120	0.370	0.832			2.149	0.370	0.900		
Fe3–S4A	2.222	2.120	0.370	0.759			2.149	0.370	0.821		
Fe3–SG	2.277	2.120	0.370	0.654	2.990	0.990	2.149	0.370	0.708	3.234	0.234
Fe4–S1	2.102	2.120	0.370	1.050			2.149	0.370	1.135		
Fe4–S3A	2.246	2.120	0.370	0.711			2.149	0.370	0.769		

Fe4–S4A	2.175	2.120	0.370	0.862			2.149	0.370	0.932		
Fe4–SG	2.223	2.120	0.370	0.757	**3.380**	1.380	2.149	0.370	0.819	3.656	0.656
Fe5–S1	2.112	2.120	0.370	1.022			2.149	0.370	1.105		
Fe5–S2B	2.231	2.120	0.370	0.741			2.149	0.370	0.801		
Fe5–S4B	2.264	2.120	0.370	0.678			2.149	0.370	0.733		
Fe5–SG	2.253	2.120	0.370	0.698	3.138	1.138	2.149	0.370	0.755	3.394	0.394
Fe6–S1	2.538	2.120	0.370	0.323			2.149	0.370	0.349		
Fe6–S2B	2.277	2.120	0.370	0.654			2.149	0.370	0.708		
Fe6–S3B	2.247	2.120	0.370	0.709			2.149	0.370	0.767		
Fe6–SG	2.264	2.120	0.370	0.678	2.364	0.364	2.149	0.370	0.733	2.557	-0.443
Fe7–S2B	2.235	2.120	0.370	0.733			2.149	0.370	0.793		
Fe7–S3B	2.242	2.120	0.370	0.719			2.149	0.370	0.778		
Fe7–S4B	2.210	2.120	0.370	0.784			2.149	0.370	0.848		
Fe7–SG	2.319	2.120	0.370	0.584	2.820	0.820	2.149	0.370	0.632	3.050	0.050
Fe8–S1	2.129	2.120	0.370	0.976			2.149	0.370	1.056		
Fe8–S3B	2.197	2.120	0.370	0.812			2.149	0.370	0.878		
Fe8–S4B	2.252	2.120	0.370	0.700			2.149	0.370	0.757		
Fe8–SG	2.197	2.120	0.370	0.812	**3.300**	1.300	2.149	0.370	0.878	3.569	0.569
					23.464					25.377	

Table S18 The abandoned valence analyses for irons in P-cluster [1] from MoFe protein 6BBL whose conformations resemble P^N but overall bond distance are on small side at 1.68 Å resolution.

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	2.282	2.120	0.370	0.645			2.149	0.370	0.698		
Fe1–S2A	2.167	2.120	0.370	0.881			2.149	0.370	0.953		
Fe1–S3A	2.135	2.120	0.370	0.960			2.149	0.370	1.039		
Fe1–SG	2.495	2.120	0.370	0.363	2.849	0.849	2.149	0.370	0.393	3.082	0.082
Fe2–S1	2.392	2.120	0.370	0.479			2.149	0.370	0.519		
Fe2–S2A	2.185	2.120	0.370	0.839			2.149	0.370	0.907		
Fe2–S4A	2.165	2.120	0.370	0.885			2.149	0.370	0.958		
Fe2–SG	2.472	2.120	0.370	0.386	2.590	0.590	2.149	0.370	0.418	2.801	-0.199
Fe3–S2A	2.183	2.120	0.370	0.843			2.149	0.370	0.912		
Fe3–S3A	2.168	2.120	0.370	0.878			2.149	0.370	0.950		
Fe3–S4A	2.185	2.120	0.370	0.839			2.149	0.370	0.907		
Fe3–SG	2.456	2.120	0.370	0.403	2.964	0.964	2.149	0.370	0.436	3.206	0.206
Fe4–S1	2.321	2.120	0.370	0.581			2.149	0.370	0.628		
Fe4–S3A	2.160	2.120	0.370	0.898			2.149	0.370	0.971		

Fe4–S4A	2.178	2.120	0.370	0.855			2.149	0.370	0.925		
Fe4–SG	2.429	2.120	0.370	0.434	2.767	0.767	2.149	0.370	0.469	2.993	-0.007
Fe5–S1	2.482	2.120	0.370	0.376			2.149	0.370	0.407		
Fe5–S2B	2.175	2.120	0.370	0.862			2.149	0.370	0.932		
Fe5–S4B	2.107	2.120	0.370	1.036			2.149	0.370	1.120		
Fe5–SG	2.485	2.120	0.370	0.373	2.646	0.646	2.149	0.370	0.403	2.862	-0.138
Fe6–S1	3.002	2.120	0.370	0.092			2.149	0.370	0.100		
Fe6–S2B	2.180	2.120	0.370	0.850			2.149	0.370	0.920		
Fe6–S3B	2.135	2.120	0.370	0.960			2.149	0.370	1.039		
Fe6–SG	2.406	2.120	0.370	0.462	2.364	0.364	2.149	0.370	0.499	2.557	-0.443
Fe7–S2B	2.180	2.120	0.370	0.850			2.149	0.370	0.920		
Fe7–S3B	2.225	2.120	0.370	0.753			2.149	0.370	0.814		
Fe7–S4B	2.211	2.120	0.370	0.782			2.149	0.370	0.846		
Fe7–SG	2.541	2.120	0.370	0.321	2.706	0.706	2.149	0.370	0.347	2.926	-0.074
Fe8–S1	2.326	2.120	0.370	0.573			2.149	0.370	0.620		
Fe8–S3B	2.172	2.120	0.370	0.869			2.149	0.370	0.940		
Fe8–S4B	2.217	2.120	0.370	0.769			2.149	0.370	0.832		
Fe8–SG	2.419	2.120	0.370	0.446	2.657	0.657	2.149	0.370	0.482	2.874	-0.126
					21.544					23.301	

Table S19 The abandoned valence analyses for irons in P-cluster [2] from MoFe protein 6BBL whose conformations resemble P^N but overall bond distance are on small side at 1.68 Å resolution.

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	2.308	2.120	0.370	0.602			2.149	0.370	0.651		
Fe1–S2A	2.162	2.120	0.370	0.893			2.149	0.370	0.965		
Fe1–S3A	2.163	2.120	0.370	0.890			2.149	0.370	0.963		
Fe1–SG	2.745	2.120	0.370	0.185	2.569	0.569	2.149	0.370	0.200	2.779	-0.221
Fe2–S1	2.425	2.120	0.370	0.439			2.149	0.370	0.474		
Fe2–S2A	2.161	2.120	0.370	0.895			2.149	0.370	0.968		
Fe2–S4A	2.141	2.120	0.370	0.945			2.149	0.370	1.022		
Fe2–SG	2.418	2.120	0.370	0.447	2.725	0.725	2.149	0.370	0.483	2.948	-0.052
Fe3–S2A	2.222	2.120	0.370	0.759			2.149	0.370	0.821		
Fe3–S3A	2.204	2.120	0.370	0.797			2.149	0.370	0.862		
Fe3–S4A	2.177	2.120	0.370	0.857			2.149	0.370	0.927		
Fe3–SG	2.391	2.120	0.370	0.481	2.894	0.894	2.149	0.370	0.520	3.130	0.130
Fe4–S1	2.362	2.120	0.370	0.520			2.149	0.370	0.562		
Fe4–S3A	2.184	2.120	0.370	0.841			2.149	0.370	0.910		
Fe4–S4A	2.168	2.120	0.370	0.878			2.149	0.370	0.950		

Fe4–SG	2.458	2.120	0.370	0.401	2.641	0.641	2.149	0.370	0.434	2.856	-0.144
Fe5–S1	2.492	2.120	0.370	0.366			2.149	0.370	0.396		
Fe5–S2B	2.181	2.120	0.370	0.848			2.149	0.370	0.917		
Fe5–S4B	2.099	2.120	0.370	1.058			2.149	0.370	1.145		
Fe5–SG	2.543	2.120	0.370	0.319	2.591	0.591	2.149	0.370	0.345	2.802	-0.198
Fe6–S1	3.020	2.120	0.370	0.088			2.149	0.370	0.095		
Fe6–S2B	2.175	2.120	0.370	0.862			2.149	0.370	0.932		
Fe6–S3B	2.127	2.120	0.370	0.981			2.149	0.370	1.061		
Fe6–SG	2.454	2.120	0.370	0.405	2.336	0.336	2.149	0.370	0.439	2.527	-0.473
Fe7–S2B	2.174	2.120	0.370	0.864			2.149	0.370	0.935		
Fe7–S3B	2.205	2.120	0.370	0.795			2.149	0.370	0.860		
Fe7–S4B	2.187	2.120	0.370	0.834			2.149	0.370	0.902		
Fe7–SG	2.513	2.120	0.370	0.346	2.839	0.839	2.149	0.370	0.374	3.070	0.070
Fe8–S1	2.329	2.120	0.370	0.568			2.149	0.370	0.615		
Fe8–S3B	2.173	2.120	0.370	0.867			2.149	0.370	0.937		
Fe8–S4B	2.213	2.120	0.370	0.778			2.149	0.370	0.841		
Fe8–SG	2.428	2.120	0.370	0.435	2.648	0.648	2.149	0.370	0.470	2.864	-0.136
					21.243					22.975	

Table S20 The abandoned valence analyses for irons in P-cluster [1] from MoFe protein 6OP1 at resolution of 1.7 Å. Faulty data in R_0 (+2) are bold highlighted.

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	2.458	2.120	0.370	0.401			2.149	0.370	0.434		
Fe1–S2A	2.015	2.120	0.370	1.328			2.149	0.370	1.436		
Fe1–S3A	2.110	2.120	0.370	1.027			2.149	0.370	1.111		
Fe1–SG	2.444	2.120	0.370	0.417	**3.173**	1.173	2.149	0.370	0.451	3.432	0.432
Fe2–S1	2.384	2.120	0.370	0.490			2.149	0.370	0.530		
Fe2–S2A	2.121	2.120	0.370	0.997			2.149	0.370	1.079		
Fe2–S4A	2.176	2.120	0.370	0.860			2.149	0.370	0.930		
Fe2–SG	2.404	2.120	0.370	0.464	2.811	0.811	2.149	0.370	0.502	3.040	0.040
Fe3–S2A	2.143	2.120	0.370	0.940			2.149	0.370	1.016		
Fe3–S3A	2.308	2.120	0.370	0.602			2.149	0.370	0.651		
Fe3–S4A	2.118	2.120	0.370	1.005			2.149	0.370	1.087		
Fe3–SG	2.355	2.120	0.370	0.530	3.077	1.077	2.149	0.370	0.573	3.327	0.327
Fe4–S1	2.410	2.120	0.370	0.457			2.149	0.370	0.494		
Fe4–S3A	2.111	2.120	0.370	1.025			2.149	0.370	1.108		
Fe4–S4A	2.145	2.120	0.370	0.935			2.149	0.370	1.011		

Fe4–SG	2.443	2.120	0.370	0.418	2.834	0.834	2.149	0.370	0.452	3.065	0.065
Fe5–S1	2.400	2.120	0.370	0.469			2.149	0.370	0.507		
Fe5–S2B	2.319	2.120	0.370	0.584			2.149	0.370	0.632		
Fe5–S4B	2.306	2.120	0.370	0.605			2.149	0.370	0.654		
Fe5–SG	2.310	2.120	0.370	0.598	2.256	0.256	2.149	0.370	0.647	2.440	-0.560
Fe6–S1	2.485	2.120	0.370	0.373			2.149	0.370	0.403		
Fe6–S2B	2.352	2.120	0.370	0.534			2.149	0.370	0.578		
Fe6–S3B	2.290	2.120	0.370	0.632			2.149	0.370	0.683		
Fe6–SG	2.341	2.120	0.370	0.550	2.089	0.089	2.149	0.370	0.595	2.259	-0.741
Fe7–S2B	2.374	2.120	0.370	0.503			2.149	0.370	0.544		
Fe7–S3B	2.324	2.120	0.370	0.576			2.149	0.370	0.623		
Fe7–S4B	2.303	2.120	0.370	0.610			2.149	0.370	0.660		
Fe7–SG	2.386	2.120	0.370	0.487	2.177	0.177	2.149	0.370	0.527	2.354	-0.646
Fe8–S1	2.348	2.120	0.370	0.540			2.149	0.370	0.584		
Fe8–S3B	2.310	2.120	0.370	0.598			2.149	0.370	0.647		
Fe8–S4B	2.301	2.120	0.370	0.613			2.149	0.370	0.663		
Fe8–SG	2.348	2.120	0.370	0.540	2.291	0.291	2.149	0.370	0.584	2.478	-0.522
					20.708					22.396	

Table S21 The abandoned valence analyses for irons in P-cluster [2] from MoFe protein 6OP1 at resolution of 1.7 Å. Faulty data in R_0 (+2) are bold highlighted.

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	2.456	2.120	0.370	0.403			2.149	0.370	0.436		
Fe1–S2A	2.160	2.120	0.370	0.898			2.149	0.370	0.971		
Fe1–S3A	2.086	2.120	0.370	1.096			2.149	0.370	1.186		
Fe1–SG	2.403	2.120	0.370	0.465	2.862	0.862	2.149	0.370	0.503	3.096	0.096
Fe2–S1	2.392	2.120	0.370	0.479			2.149	0.370	0.519		
Fe2–S2A	2.188	2.120	0.370	0.832			2.149	0.370	0.900		
Fe2–S4A	2.172	2.120	0.370	0.869			2.149	0.370	0.940		
Fe2–SG	2.406	2.120	0.370	0.462	2.642	0.642	2.149	0.370	0.499	2.857	-0.143
Fe3–S2A	2.102	2.120	0.370	1.050			2.149	0.370	1.135		
Fe3–S3A	2.332	2.120	0.370	0.564			2.149	0.370	0.610		
Fe3–S4A	2.131	2.120	0.370	0.971			2.149	0.370	1.050		
Fe3–SG	2.395	2.120	0.370	0.476	3.060	1.060	2.149	0.370	0.514	3.309	0.309
Fe4–S1	2.396	2.120	0.370	0.474			2.149	0.370	0.513		
Fe4–S3A	2.103	2.120	0.370	1.047			2.149	0.370	1.132		

Fe4–S4A	2.038	2.120	0.370	1.248			2.149	0.370	1.350		
Fe4–SG	2.477	2.120	0.370	0.381	**3.150**	1.150	2.149	0.370	0.412	3.407	0.407
Fe5–S1	2.440	2.120	0.370	0.421			2.149	0.370	0.455		
Fe5–S2B	2.299	2.120	0.370	0.616			2.149	0.370	0.667		
Fe5–S4B	2.314	2.120	0.370	0.592			2.149	0.370	0.640		
Fe5–SG	2.333	2.120	0.370	0.562	2.192	0.192	2.149	0.370	0.608	2.371	-0.629
Fe6–S1	2.494	2.120	0.370	0.364			2.149	0.370	0.394		
Fe6–S2B	2.353	2.120	0.370	0.533			2.149	0.370	0.576		
Fe6–S3B	2.274	2.120	0.370	0.660			2.149	0.370	0.713		
Fe6–SG	2.347	2.120	0.370	0.541	2.098	0.098	2.149	0.370	0.586	2.269	-0.731
Fe7–S2B	2.353	2.120	0.370	0.533			2.149	0.370	0.576		
Fe7–S3B	2.316	2.120	0.370	0.589			2.149	0.370	0.637		
Fe7–S4B	2.299	2.120	0.370	0.616			2.149	0.370	0.667		
Fe7–SG	2.390	2.120	0.370	0.482	2.220	0.220	2.149	0.370	0.521	2.401	-0.599
Fe8–S1	2.359	2.120	0.370	0.524			2.149	0.370	0.567		
Fe8–S3B	2.288	2.120	0.370	0.635			2.149	0.370	0.687		
Fe8–S4B	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe8–SG	2.382	2.120	0.370	0.493	2.292	0.292	2.149	0.370	0.533	2.479	-0.521
					20.516					22.189	

Table S22 The abandoned valence analyses for irons in P-cluster [1] from MoFe protein 6OP2 at resolution of 1.9 Å. Faulty data in R_0 (+2) are bold highlighted.

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	2.477	2.120	0.370	0.381			2.149	0.370	0.412		
Fe1–S2A	2.141	2.120	0.370	0.945			2.149	0.370	1.022		
Fe1–S3A	2.025	2.120	0.370	1.293			2.149	0.370	1.398		
Fe1–SG	2.458	2.120	0.370	0.401	3.061	1.061	2.149	0.370	0.434	3.136	0.136
Fe2–S1	2.375	2.120	0.370	0.502			2.149	0.370	0.543		
Fe2–S2A	2.167	2.120	0.370	0.881			2.149	0.370	0.953		
Fe2–S4A	2.089	2.120	0.370	1.087			2.149	0.370	1.176		
Fe2–SG	2.445	2.120	0.370	0.415	2.925	0.925	2.149	0.370	0.449	2.997	-0.003
Fe3–S2A	1.988	2.120	0.370	1.429			2.149	0.370	1.545		
Fe3–S3A	2.351	2.120	0.370	0.536			2.149	0.370	0.579		
Fe3–S4A	2.039	2.120	0.370	1.245			2.149	0.370	1.346		
Fe3–SG	2.390	2.120	0.370	0.482	**3.741**	1.741	2.149	0.370	0.521	3.833	0.833
Fe4–S1	2.351	2.120	0.370	0.536			2.149	0.370	0.579		
Fe4–S3A	2.024	2.120	0.370	1.296			2.149	0.370	1.402		

Fe4–S4A	1.976	2.120	0.370	1.476			2.149	0.370	1.596		
Fe4–SG	2.436	2.120	0.370	0.426	**3.784**	1.784	2.149	0.370	0.460	3.877	0.877
Fe5–S1	2.381	2.120	0.370	0.494			2.149	0.370	0.534		
Fe5–S2B	2.368	2.120	0.370	0.512			2.149	0.370	0.553		
Fe5–S4B	2.290	2.120	0.370	0.632			2.149	0.370	0.683		
Fe5–SG	2.316	2.120	0.370	0.589	2.256	0.256	2.149	0.370	0.637	2.312	-0.688
Fe6–S1	2.555	2.120	0.370	0.309			2.149	0.370	0.334		
Fe6–S2B	2.447	2.120	0.370	0.413			2.149	0.370	0.447		
Fe6–S3B	2.251	2.120	0.370	0.702			2.149	0.370	0.759		
Fe6–SG	2.394	2.120	0.370	0.477	1.926	-0.074	2.149	0.370	0.516	1.974	-1.026
Fe7–S2B	2.368	2.120	0.370	0.512			2.149	0.370	0.553		
Fe7–S3B	2.360	2.120	0.370	0.523			2.149	0.370	0.565		
Fe7–S4B	2.317	2.120	0.370	0.587			2.149	0.370	0.635		
Fe7–SG	2.351	2.120	0.370	0.536	2.186	0.186	2.149	0.370	0.579	2.240	-0.760
Fe8–S1	2.371	2.120	0.370	0.507			2.149	0.370	0.549		
Fe8–S3B	2.301	2.120	0.370	0.613			2.149	0.370	0.663		
Fe8–S4B	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe8–SG	2.387	2.120	0.370	0.486	2.279	0.279	2.149	0.370	0.526	2.335	-0.665
					22.159					22.705	

Table S23 The abandoned valence analyses for irons in P-cluster [2] from MoFe protein 6OP2 at resolution of 1.9 Å. Faulty data in R_0 (+2) are bold highlighted.

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	2.450	2.120	0.370	0.410			2.149	0.370	0.443		
Fe1–S2A	1.916	2.120	0.370	1.736			2.149	0.370	1.877		
Fe1–S3A	1.993	2.120	0.370	1.410			2.149	0.370	1.524		
Fe1–SG	2.425	2.120	0.370	0.439	**3.994**	1.994	2.149	0.370	0.474	4.319	1.319
Fe2–S1	2.416	2.120	0.370	0.449			2.149	0.370	0.486		
Fe2–S2A	2.016	2.120	0.370	1.325			2.149	0.370	1.433		
Fe2–S4A	2.113	2.120	0.370	1.019			2.149	0.370	1.102		
Fe2–SG	2.422	2.120	0.370	0.442	**3.235**	1.235	2.149	0.370	0.478	3.499	0.499
Fe3–S2A	2.103	2.120	0.370	1.047			2.149	0.370	1.132		
Fe3–S3A	2.206	2.120	0.370	0.793			2.149	0.370	0.857		
Fe3–S4A	1.993	2.120	0.370	1.410			2.149	0.370	1.524		
Fe3–SG	2.356	2.120	0.370	0.528	**3.778**	1.778	2.149	0.370	0.572	4.086	1.086
Fe4–S1	2.344	2.120	0.370	0.546			2.149	0.370	0.590		
Fe4–S3A	2.020	2.120	0.370	1.310			2.149	0.370	1.417		

Fe4–S4A	2.061	2.120	0.370	1.173			2.149	0.370	1.269		
Fe4–SG	2.403	2.120	0.370	0.465	**3.494**	1.494	2.149	0.370	0.503	3.779	0.779
Fe5–S1	2.345	2.120	0.370	0.544			2.149	0.370	0.589		
Fe5–S2B	2.326	2.120	0.370	0.573			2.149	0.370	0.620		
Fe5–S4B	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe5–SG	2.319	2.120	0.370	0.584	2.343	0.343	2.149	0.370	0.632	2.534	-0.466
Fe6–S1	2.498	2.120	0.370	0.360			2.149	0.370	0.389		
Fe6–S2B	2.380	2.120	0.370	0.495			2.149	0.370	0.536		
Fe6–S3B	2.267	2.120	0.370	0.672			2.149	0.370	0.727		
Fe6–SG	2.406	2.120	0.370	0.462	1.989	-0.011	2.149	0.370	0.499	2.151	-0.849
Fe7–S2B	2.332	2.120	0.370	0.564			2.149	0.370	0.610		
Fe7–S3B	2.365	2.120	0.370	0.516			2.149	0.370	0.558		
Fe7–S4B	2.340	2.120	0.370	0.552			2.149	0.370	0.597		
Fe7–SG	2.325	2.120	0.370	0.575	2.206	0.206	2.149	0.370	0.621	2.386	-0.614
Fe8–S1	2.340	2.120	0.370	0.552			2.149	0.370	0.597		
Fe8–S3B	2.274	2.120	0.370	0.660			2.149	0.370	0.713		
Fe8–S4B	2.274	2.120	0.370	0.660			2.149	0.370	0.713		
Fe8–SG	2.414	2.120	0.370	0.452	2.323	0.323	2.149	0.370	0.489	2.512	-0.488
					23.362					25.266	

Table S24 The abandoned valence analyses for irons in P-cluster [1] from MoFe protein 6OP4 at resolution of 2.3 Å. Faulty data in R_0 (+2) are bold highlighted.

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	2.477	2.12	0.37	0.381			2.149	0.37	0.412		
Fe1–S2A	2.156	2.12	0.37	0.907			2.149	0.37	0.981		
Fe1–S3A	1.989	2.12	0.37	1.425			2.149	0.37	1.541		
Fe1–SG	2.374	2.12	0.37	0.503	**3.216**	1.216	2.149	0.37	0.544	3.479	0.479
Fe2–S1	2.411	2.12	0.37	0.455			2.149	0.37	0.493		
Fe2–S2A	2.122	2.12	0.37	0.995			2.149	0.37	1.076		
Fe2–S4A	2.053	2.12	0.37	1.199			2.149	0.37	1.296		
Fe2–SG	2.442	2.12	0.37	0.419	3.067	1.067	2.149	0.37	0.453	3.317	0.317
Fe3–S2A	2.021	2.12	0.37	1.307			2.149	0.37	1.413		
Fe3–S3A	2.174	2.12	0.37	0.864			2.149	0.37	0.935		
Fe3–S4A	2.050	2.12	0.37	1.208			2.149	0.37	1.307		
Fe3–SG	2.358	2.12	0.37	0.526	**3.905**	1.905	2.149	0.37	0.568	4.223	1.223
Fe4–S1	2.360	2.12	0.37	0.523			2.149	0.37	0.565		
Fe4–S3A	1.997	2.12	0.37	1.394			2.149	0.37	1.508		

Fe4–S4A	2.028	2.12	0.37	1.282			2.149	0.37	1.387		
Fe4–SG	2.321	2.12	0.37	0.581	**3.780**	1.780	2.149	0.37	0.628	4.088	1.088
Fe5–S1	2.405	2.12	0.37	0.463			2.149	0.37	0.501		
Fe5–S2B	2.326	2.12	0.37	0.573			2.149	0.37	0.620		
Fe5–S4B	2.257	2.12	0.37	0.691			2.149	0.37	0.747		
Fe5–SG	2.405	2.12	0.37	0.463	2.189	0.189	2.149	0.37	0.501	2.368	-0.632
Fe6–S1	2.550	2.12	0.37	0.313			2.149	0.37	0.338		
Fe6–S2B	2.414	2.12	0.37	0.452			2.149	0.37	0.489		
Fe6–S3B	2.274	2.12	0.37	0.660			2.149	0.37	0.713		
Fe6–SG	2.328	2.12	0.37	0.570	1.994	-0.006	2.149	0.37	0.616	2.157	-0.843
Fe7–S2B	2.340	2.12	0.37	0.552			2.149	0.37	0.597		
Fe7–S3B	2.285	2.12	0.37	0.640			2.149	0.37	0.692		
Fe7–S4B	2.299	2.12	0.37	0.616			2.149	0.37	0.667		
Fe7–SG	2.323	2.12	0.37	0.578	2.386	0.386	2.149	0.37	0.625	2.581	-0.419
Fe8–S1	2.364	2.12	0.37	0.517			2.149	0.37	0.559		
Fe8–S3B	2.256	2.12	0.37	0.692			2.149	0.37	0.749		
Fe8–S4B	2.267	2.12	0.37	0.672			2.149	0.37	0.727		
Fe8–SG	2.224	2.12	0.37	0.755	2.637	0.637	2.149	0.37	0.817	2.852	-0.148
					23.175					25.065	

Table S25 The abandoned valence analyses for irons in P-cluster [2] from MoFe protein 6OP4 at resolution of 2.3 Å. Faulty data in R_0 (+2) are bold highlighted.

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	2.443	2.120	0.370	0.418			2.149	0.37	0.452		
Fe1–S2A	1.508	2.120	0.370	5.228			2.149	0.37	5.654		
Fe1–S3A	1.920	2.120	0.370	1.717			2.149	0.37	1.857		
Fe1–SG	2.369	2.120	0.370	0.510	**7.873**	5.873	2.149	0.37	0.552	8.515	5.515
Fe2–S1	2.448	2.120	0.370	0.412			2.149	0.37	0.446		
Fe2–S2A	1.956	2.120	0.370	1.558			2.149	0.37	1.685		
Fe2–S4A	2.063	2.120	0.370	1.167			2.149	0.37	1.262		
Fe2–SG	2.397	2.120	0.370	0.473	**3.609**	1.609	2.149	0.37	0.512	3.904	0.904
Fe3–S2A	2.205	2.120	0.370	0.795			2.149	0.37	0.860		
Fe3–S3A	2.188	2.120	0.370	0.832			2.149	0.37	0.900		
Fe3–S4A	1.961	2.120	0.370	1.537			2.149	0.37	1.662		
Fe3–SG	2.258	2.120	0.370	0.689	**3.852**	1.852	2.149	0.37	0.745	4.166	1.166
Fe4–S1	2.371	2.120	0.370	0.507			2.149	0.37	0.549		
Fe4–S3A	1.986	2.120	0.370	1.436			2.149	0.37	1.554		

Fe4–S4A	1.975	2.120	0.370	1.480			2.149	0.37	1.600		
Fe4–SG	2.377	2.120	0.370	0.499	**3.923**	1.923	2.149	0.37	0.540	4.243	1.243
Fe5–S1	2.300	2.120	0.370	0.615			2.149	0.37	0.665		
Fe5–S2B	2.392	2.120	0.370	0.479			2.149	0.37	0.519		
Fe5–S4B	2.210	2.120	0.370	0.784			2.149	0.37	0.848		
Fe5–SG	2.271	2.120	0.370	0.665	2.543	0.543	2.149	0.37	0.719	2.751	-0.249
Fe6–S1	2.438	2.120	0.370	0.423			2.149	0.37	0.458		
Fe6–S2B	2.449	2.120	0.370	0.411			2.149	0.37	0.444		
Fe6–S3B	2.282	2.120	0.370	0.645			2.149	0.37	0.698		
Fe6–SG	2.407	2.120	0.370	0.460	1.940	-0.060	2.149	0.37	0.498	2.098	-0.902
Fe7–S2B	2.287	2.120	0.370	0.637			2.149	0.37	0.689		
Fe7–S3B	2.329	2.120	0.370	0.568			2.149	0.37	0.615		
Fe7–S4B	2.361	2.120	0.370	0.521			2.149	0.37	0.564		
Fe7–SG	2.404	2.120	0.370	0.464	2.191	0.191	2.149	0.37	0.502	2.369	-0.631
Fe8–S1	2.314	2.120	0.370	0.592			2.149	0.37	0.640		
Fe8–S3B	2.291	2.120	0.370	0.630			2.149	0.37	0.681		
Fe8–S4B	2.291	2.120	0.370	0.630			2.149	0.37	0.681		
Fe8–SG	2.293	2.120	0.370	0.627	2.478	0.478	2.149	0.37	0.678	2.680	-0.320
					28.410					30.726	

Table S26 The adopted bond valence analyses for irons in P-cluster [1] from MoFe protein 1H1L which was reported as P^N at 1.9 Å resolution.

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	2.447	2.12	0.37	0.413			2.149	0.37	0.447		
Fe1–S2A	2.330	2.12	0.37	0.567			2.149	0.37	0.613		
Fe1–S3A	2.331	2.12	0.37	0.565			2.149	0.37	0.611		
Fe1–SG	2.354	2.12	0.37	0.531	2.077	0.077	2.149	0.37	0.575	2.246	-0.754
Fe2–S1	2.496	2.12	0.37	0.362			2.149	0.37	0.391		
Fe2–S2A	2.353	2.12	0.37	0.533			2.149	0.37	0.576		
Fe2–S4A	2.280	2.12	0.37	0.649			2.149	0.37	0.702		
Fe2–SG	2.306	2.12	0.37	0.605	2.149	0.149	2.149	0.37	0.654	2.324	-0.676
Fe3–S2A	2.328	2.12	0.37	0.570			2.149	0.37	0.616		
Fe3–S3A	2.345	2.12	0.37	0.544			2.149	0.37	0.589		
Fe3–S4A	2.326	2.12	0.37	0.573			2.149	0.37	0.620		
Fe3–SG	2.291	2.12	0.37	0.630	2.317	0.317	2.149	0.37	0.681	2.506	-0.494
Fe4–S1	2.473	2.12	0.37	0.385			2.149	0.37	0.417		
Fe4–S3A	2.329	2.12	0.37	0.568			2.149	0.37	0.615		
Fe4–S4A	2.243	2.12	0.37	0.717			2.149	0.37	0.776		

Fe4–SG	2.268	2.12	0.37	0.670	2.341	0.341	2.149	0.37	0.725	2.532	-0.468
Fe5–S1	2.460	2.12	0.37	0.399			2.149	0.37	0.431		
Fe5–S2B	2.350	2.12	0.37	0.537			2.149	0.37	0.581		
Fe5–S4B	2.356	2.12	0.37	0.528			2.149	0.37	0.572		
Fe5–SG	2.357	2.12	0.37	0.527	1.991	-0.009	2.149	0.37	0.570	2.154	-0.846
Fe6–S1	2.477	2.12	0.37	0.381			2.149	0.37	0.412		
Fe6–S2B	2.337	2.12	0.37	0.556			2.149	0.37	0.602		
Fe6–S3B	2.342	2.12	0.37	0.549			2.149	0.37	0.594		
Fe6–SG	2.339	2.12	0.37	0.553	2.039	0.039	2.149	0.37	0.598	2.206	-0.794
Fe7–S2B	2.323	2.12	0.37	0.578			2.149	0.37	0.625		
Fe7–S3B	2.407	2.12	0.37	0.460			2.149	0.37	0.498		
Fe7–S4B	2.328	2.12	0.37	0.570			2.149	0.37	0.616		
Fe7–SG	2.306	2.12	0.37	0.605	2.213	0.213	2.149	0.37	0.654	2.393	-0.607
Fe8–S1	2.446	2.12	0.37	0.414			2.149	0.37	0.448		
Fe8–S3B	2.387	2.12	0.37	0.486			2.149	0.37	0.526		
Fe8–S4B	2.289	2.12	0.37	0.634			2.149	0.37	0.685		
Fe8–SG	2.254	2.12	0.37	0.696	2.230	0.230	2.149	0.37	0.753	2.412	-0.588
					17.358					18.773	

Table S27 The adopted bond valence analyses for irons in P-cluster [2] from MoFe protein 1H1L which was reported as P^N at 1.9 Å resolution.

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	2.472	2.12	0.37	0.386			2.149	0.37	0.418		
Fe1–S2A	2.331	2.12	0.37	0.565			2.149	0.37	0.611		
Fe1–S3A	2.299	2.12	0.37	0.616			2.149	0.37	0.667		
Fe1–SG	2.353	2.12	0.37	0.533	2.101	0.101	2.149	0.37	0.576	2.272	-0.728
Fe2–S1	2.472	2.12	0.37	0.386			2.149	0.37	0.418		
Fe2–S2A	2.326	2.12	0.37	0.573			2.149	0.37	0.620		
Fe2–S4A	2.267	2.12	0.37	0.672			2.149	0.37	0.727		
Fe2–SG	2.313	2.12	0.37	0.594	2.225	0.225	2.149	0.37	0.642	2.406	-0.594
Fe3–S2A	2.374	2.12	0.37	0.503			2.149	0.37	0.544		
Fe3–S3A	2.294	2.12	0.37	0.625			2.149	0.37	0.676		
Fe3–S4A	2.313	2.12	0.37	0.594			2.149	0.37	0.642		
Fe3–SG	2.206	2.12	0.37	0.793	2.514	0.514	2.149	0.37	0.857	2.719	-0.281
Fe4–S1	2.447	2.12	0.37	0.413			2.149	0.37	0.447		
Fe4–S3A	2.332	2.12	0.37	0.564			2.149	0.37	0.610		
Fe4–S4A	2.206	2.12	0.37	0.793			2.149	0.37	0.857		
Fe4–SG	2.269	2.12	0.37	0.669	2.438	0.438	2.149	0.37	0.723	2.637	-0.363

Fe5–S1	2.453	2.12	0.37	0.407			2.149	0.37	0.440		
Fe5–S2B	2.312	2.12	0.37	0.595			2.149	0.37	0.644		
Fe5–S4B	2.361	2.12	0.37	0.521			2.149	0.37	0.564		
Fe5–SG	2.311	2.12	0.37	0.597	2.120	0.120	2.149	0.37	0.645	2.293	-0.707
Fe6–S1	2.509	2.12	0.37	0.349			2.149	0.37	0.378		
Fe6–S2B	2.372	2.12	0.37	0.506			2.149	0.37	0.547		
Fe6–S3B	2.350	2.12	0.37	0.537			2.149	0.37	0.581		
Fe6–SG	2.327	2.12	0.37	0.572	1.964	-0.036	2.149	0.37	0.618	2.124	-0.876
Fe7–S2B	2.368	2.12	0.37	0.512			2.149	0.37	0.553		
Fe7–S3B	2.379	2.12	0.37	0.497			2.149	0.37	0.537		
Fe7–S4B	2.351	2.12	0.37	0.536			2.149	0.37	0.579		
Fe7–SG	2.311	2.12	0.37	0.597	2.141	0.141	2.149	0.37	0.645	2.315	-0.685
Fe8–S1	2.411	2.12	0.37	0.455			2.149	0.37	0.493		
Fe8–S3B	2.351	2.12	0.37	0.536			2.149	0.37	0.579		
Fe8–S4B	2.320	2.12	0.37	0.582			2.149	0.37	0.630		
Fe8–SG	2.273	2.12	0.37	0.661	2.235	0.235	2.149	0.37	0.715	2.417	-0.583
					17.738					19.184	

Table S28 The adopted bond valence analyses for irons in P-cluster from MoFe protein 1L5H which was reported as P^N at 2.3 Å resolution.

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	2.264	2.120	0.370	0.678			2.149	0.370	0.733		
Fe1–S2A	2.146	2.120	0.370	0.932			2.149	0.370	1.008		
Fe1–S3A	2.248	2.120	0.370	0.708			2.149	0.370	0.765		
Fe1–SG	2.378	2.120	0.370	0.498	2.815	0.815	2.149	0.370	0.539	3.045	0.045
Fe2–S1	2.330	2.120	0.370	0.567			2.149	0.370	0.613		
Fe2–S2A	2.198	2.120	0.370	0.810			2.149	0.370	0.876		
Fe2–S4A	2.308	2.120	0.370	0.602			2.149	0.370	0.651		
Fe2–SG	2.326	2.120	0.370	0.573	2.552	0.552	2.149	0.370	0.620	2.760	-0.240
Fe3–S2A	2.364	2.120	0.370	0.517			2.149	0.370	0.559		
Fe3–S3A	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe3–S4A	2.239	2.120	0.370	0.725			2.149	0.370	0.784		
Fe3–SG	2.385	2.120	0.370	0.489	2.367	0.367	2.149	0.370	0.528	2.560	-0.440
Fe4–S1	2.328	2.120	0.370	0.570			2.149	0.370	0.616		
Fe4–S3A	2.286	2.120	0.370	0.638			2.149	0.370	0.691		
Fe4–S4A	2.297	2.120	0.370	0.620			2.149	0.370	0.670		

Fe4–SG	2.400	2.120	0.370	0.469	2.297	0.297	2.149	0.370	0.507	2.485	-0.515
Fe5–S1	2.359	2.120	0.370	0.524			2.149	0.370	0.567		
Fe5–S2B	2.311	2.120	0.370	0.597			2.149	0.370	0.645		
Fe5–S4B	2.254	2.120	0.370	0.696			2.149	0.370	0.753		
Fe5–SG	2.423	2.120	0.370	0.441	2.258	0.258	2.149	0.370	0.477	2.442	-0.558
Fe6–S1	2.732	2.120	0.370	0.191			2.149	0.370	0.207		
Fe6–S2B	2.349	2.120	0.370	0.539			2.149	0.370	0.582		
Fe6–S3B	2.261	2.120	0.370	0.683			2.149	0.370	0.739		
Fe6–SG	2.488	2.120	0.370	0.370	1.783	-0.217	2.149	0.370	0.400	1.928	-1.072
Fe7–S2B	2.293	2.120	0.370	0.627			2.149	0.370	0.678		
Fe7–S3B	2.291	2.120	0.370	0.630			2.149	0.370	0.681		
Fe7–S4B	2.290	2.120	0.370	0.632			2.149	0.370	0.683		
Fe7–SG	2.278	2.120	0.370	0.652	2.541	0.541	2.149	0.370	0.706	2.748	-0.252
Fe8–S1	2.369	2.120	0.370	0.510			2.149	0.370	0.552		
Fe8–S3B	2.300	2.120	0.370	0.615			2.149	0.370	0.665		
Fe8–S4B	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe8–SG	2.285	2.120	0.370	0.640	2.402	0.402	2.149	0.370	0.692	2.598	-0.402
					19.015					20.565	

Table S29 The adopted bond valence analyses for irons in P-cluster [1] from MoFe protein 1M1N which was reported as P^N at 1.16Å resolution.

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	2.483	2.12	0.37	0.375			2.149	0.37	0.405		
Fe1–S2A	2.286	2.12	0.37	0.638			2.149	0.37	0.691		
Fe1–S3A	2.281	2.12	0.37	0.647			2.149	0.37	0.700		
Fe1–SG	2.350	2.12	0.37	0.537	2.198	0.198	2.149	0.37	0.581	2.377	-0.623
Fe2–S1	2.446	2.12	0.37	0.414			2.149	0.37	0.448		
Fe2–S2A	2.313	2.12	0.37	0.594			2.149	0.37	0.642		
Fe2–S4A	2.316	2.12	0.37	0.589			2.149	0.37	0.637		
Fe2–SG	2.309	2.12	0.37	0.600	2.197	0.197	2.149	0.37	0.649	2.376	-0.624
Fe3–S2A	2.319	2.12	0.37	0.584			2.149	0.37	0.632		
Fe3–S3A	2.278	2.12	0.37	0.652			2.149	0.37	0.706		
Fe3–S4A	2.337	2.12	0.37	0.556			2.149	0.37	0.602		
Fe3–SG	2.289	2.12	0.37	0.633	2.426	0.426	2.149	0.37	0.685	2.624	-0.376
Fe4–S1	2.401	2.12	0.37	0.468			2.149	0.37	0.506		
Fe4–S3A	2.269	2.12	0.37	0.669			2.149	0.37	0.723		
Fe4–S4A	2.266	2.12	0.37	0.674			2.149	0.37	0.729		

Fe4–SG	2.339	2.12	0.37	0.553	2.364	0.364	2.149	0.37	0.598	2.556	-0.444
Fe5–S1	2.426	2.12	0.37	0.437			2.149	0.37	0.473		
Fe5–S2B	2.296	2.12	0.37	0.621			2.149	0.37	0.672		
Fe5–S4B	2.278	2.12	0.37	0.652			2.149	0.37	0.706		
Fe5–SG	2.384	2.12	0.37	0.490	2.201	0.201	2.149	0.37	0.530	2.381	-0.619
Fe6–S1	2.453	2.12	0.37	0.407			2.149	0.37	0.440		
Fe6–S2B	2.349	2.12	0.37	0.539			2.149	0.37	0.582		
Fe6–S3B	2.348	2.12	0.37	0.540			2.149	0.37	0.584		
Fe6–SG	2.313	2.12	0.37	0.594	2.079	0.079	2.149	0.37	0.642	2.248	-0.752
Fe7–S2B	2.341	2.12	0.37	0.550			2.149	0.37	0.595		
Fe7–S3B	2.351	2.12	0.37	0.536			2.149	0.37	0.579		
Fe7–S4B	2.314	2.12	0.37	0.592			2.149	0.37	0.640		
Fe7–SG	2.307	2.12	0.37	0.603	2.281	0.281	2.149	0.37	0.652	2.467	-0.533
Fe8–S1	2.435	2.12	0.37	0.427			2.149	0.37	0.462		
Fe8–S3B	2.280	2.12	0.37	0.649			2.149	0.37	0.702		
Fe8–S4B	2.277	2.12	0.37	0.654			2.149	0.37	0.708		
Fe8–SG	2.329	2.12	0.37	0.568	2.298	0.298	2.149	0.37	0.615	2.486	-0.514
					18.043					19.515	

Table S30 The adopted bond valence analyses for irons in P-cluster [2] from MoFe protein 1M1N which was reported as P^N at 1.16 Å resolution.

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	2.483	2.120	0.370	0.375			2.149	0.370	0.405		
Fe1–S2A	2.283	2.120	0.370	0.644			2.149	0.370	0.696		
Fe1–S3A	2.270	2.120	0.370	0.667			2.149	0.370	0.721		
Fe1–SG	2.348	2.120	0.370	0.540	2.225	0.225	2.149	0.370	0.584	2.407	-0.593
Fe2–S1	2.438	2.120	0.370	0.423			2.149	0.370	0.458		
Fe2–S2A	2.305	2.120	0.370	0.607			2.149	0.370	0.656		
Fe2–S4A	2.321	2.120	0.370	0.581			2.149	0.370	0.628		
Fe2–SG	2.295	2.120	0.370	0.623	2.234	0.234	2.149	0.370	0.674	2.416	-0.584
Fe3–S2A	2.318	2.120	0.370	0.586			2.149	0.370	0.633		
Fe3–S3A	2.267	2.120	0.370	0.672			2.149	0.370	0.727		
Fe3–S4A	2.356	2.120	0.370	0.528			2.149	0.370	0.572		
Fe3–SG	2.295	2.120	0.370	0.623	2.409	0.409	2.149	0.370	0.674	2.606	-0.394
Fe4–S1	2.392	2.120	0.370	0.479			2.149	0.370	0.519		
Fe4–S3A	2.256	2.120	0.370	0.692			2.149	0.370	0.749		
Fe4–S4A	2.296	2.120	0.370	0.621			2.149	0.370	0.672		

Fe4–SG	2.320	2.120	0.370	0.582	2.376	0.376	2.149	0.370	0.630	2.569	-0.431
Fe5–S1	2.426	2.120	0.370	0.437			2.149	0.370	0.473		
Fe5–S2B	2.315	2.120	0.370	0.590			2.149	0.370	0.638		
Fe5–S4B	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe5–SG	2.366	2.120	0.370	0.514	2.182	0.182	2.149	0.370	0.556	2.360	-0.640
Fe6–S1	2.459	2.120	0.370	0.400			2.149	0.370	0.433		
Fe6–S2B	2.343	2.120	0.370	0.547			2.149	0.370	0.592		
Fe6–S3B	2.329	2.120	0.370	0.568			2.149	0.370	0.615		
Fe6–SG	2.320	2.120	0.370	0.582	2.098	0.098	2.149	0.370	0.630	2.269	-0.731
Fe7–S2B	2.347	2.120	0.370	0.541			2.149	0.370	0.586		
Fe7–S3B	2.331	2.120	0.370	0.565			2.149	0.370	0.611		
Fe7–S4B	2.315	2.120	0.370	0.590			2.149	0.370	0.638		
Fe7–SG	2.347	2.120	0.370	0.541	2.239	0.239	2.149	0.370	0.586	2.421	-0.579
Fe8–S1	2.444	2.120	0.370	0.417			2.149	0.370	0.451		
Fe8–S3B	2.315	2.120	0.370	0.590			2.149	0.370	0.638		
Fe8–S4B	2.266	2.120	0.370	0.674			2.149	0.370	0.729		
Fe8–SG	2.301	2.120	0.370	0.613	2.294	0.294	2.149	0.370	0.663	2.481	-0.519
					18.057					19.530	

Table S31 The adopted bond valence analyses for irons in P-cluster [3] from MoFe protein 1M1N which was reported as P^N at 1.16 Å resolution.

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	2.488	2.120	0.370	0.370			2.149	0.370	0.400		
Fe1–S2A	2.271	2.120	0.370	0.665			2.149	0.370	0.719		
Fe1–S3A	2.288	2.120	0.370	0.635			2.149	0.370	0.687		
Fe1–SG	2.347	2.120	0.370	0.541	2.211	0.211	2.149	0.370	0.586	2.392	-0.608
Fe2–S1	2.450	2.120	0.370	0.410			2.149	0.370	0.443		
Fe2–S2A	2.309	2.120	0.370	0.600			2.149	0.370	0.649		
Fe2–S4A	2.309	2.120	0.370	0.600			2.149	0.370	0.649		
Fe2–SG	2.313	2.120	0.370	0.594	2.203	0.203	2.149	0.370	0.642	2.383	-0.617
Fe3–S2A	2.321	2.120	0.370	0.581			2.149	0.370	0.628		
Fe3–S3A	2.268	2.120	0.370	0.670			2.149	0.370	0.725		
Fe3–S4A	2.331	2.120	0.370	0.565			2.149	0.370	0.611		
Fe3–SG	2.295	2.120	0.370	0.623	2.440	0.440	2.149	0.370	0.674	2.639	-0.361
Fe4–S1	2.401	2.120	0.370	0.468			2.149	0.370	0.506		
Fe4–S3A	2.283	2.120	0.370	0.644			2.149	0.370	0.696		
Fe4–S4A	2.270	2.120	0.370	0.667			2.149	0.370	0.721		

Fe4–SG	2.336	2.120	0.370	0.558	2.336	0.336	2.149	0.370	0.603	2.527	-0.473
Fe5–S1	2.427	2.120	0.370	0.436			2.149	0.370	0.472		
Fe5–S2B	2.282	2.120	0.370	0.645			2.149	0.370	0.698		
Fe5–S4B	2.275	2.120	0.370	0.658			2.149	0.370	0.711		
Fe5–SG	2.378	2.120	0.370	0.498	2.237	0.237	2.149	0.370	0.539	2.420	-0.580
Fe6–S1	2.444	2.120	0.370	0.417			2.149	0.370	0.451		
Fe6–S2B	2.340	2.120	0.370	0.552			2.149	0.370	0.597		
Fe6–S3B	2.355	2.120	0.370	0.530			2.149	0.370	0.573		
Fe6–SG	2.304	2.120	0.370	0.608	2.106	0.106	2.149	0.370	0.658	2.278	-0.722
Fe7–S2B	2.341	2.120	0.370	0.550			2.149	0.370	0.595		
Fe7–S3B	2.343	2.120	0.370	0.547			2.149	0.370	0.592		
Fe7–S4B	2.313	2.120	0.370	0.594			2.149	0.370	0.642		
Fe7–SG	2.299	2.120	0.370	0.616	2.308	0.308	2.149	0.370	0.667	2.496	-0.504
Fe8–S1	2.430	2.120	0.370	0.433			2.149	0.370	0.468		
Fe8–S3B	2.290	2.120	0.370	0.632			2.149	0.370	0.683		
Fe8–S4B	2.282	2.120	0.370	0.645			2.149	0.370	0.698		
Fe8–SG	2.331	2.120	0.370	0.565	2.275	0.275	2.149	0.370	0.611	2.461	-0.539
					18.117					19.594	

Table S32 The adopted bond valence analyses for irons in P-cluster [4] from MoFe protein 1M1N which was reported as P^N at 1.16 Å resolution.

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	2.493	2.120	0.370	0.365			2.149	0.370	0.395		
Fe1–S2A	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe1–S3A	2.269	2.120	0.370	0.669			2.149	0.370	0.723		
Fe1–SG	2.338	2.120	0.370	0.555	2.241	0.241	2.149	0.370	0.600	2.423	-0.577
Fe2–S1	2.440	2.120	0.370	0.421			2.149	0.370	0.455		
Fe2–S2A	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe2–S4A	2.317	2.120	0.370	0.587			2.149	0.370	0.635		
Fe2–SG	2.300	2.120	0.370	0.615	2.260	0.260	2.149	0.370	0.665	2.444	-0.556
Fe3–S2A	2.311	2.120	0.370	0.597			2.149	0.370	0.645		
Fe3–S3A	2.270	2.120	0.370	0.667			2.149	0.370	0.721		
Fe3–S4A	2.345	2.120	0.370	0.544			2.149	0.370	0.589		
Fe3–SG	2.266	2.120	0.370	0.674	2.482	0.482	2.149	0.370	0.729	2.684	-0.316
Fe4–S1	2.393	2.120	0.370	0.478			2.149	0.370	0.517		
Fe4–S3A	2.264	2.120	0.370	0.678			2.149	0.370	0.733		
Fe4–S4A	2.289	2.120	0.370	0.633			2.149	0.370	0.685		

Fe4–SG	2.307	2.120	0.370	0.603	2.392	0.392	2.149	0.370	0.652	2.587	-0.413
Fe5–S1	2.441	2.120	0.370	0.420			2.149	0.370	0.454		
Fe5–S2B	2.316	2.120	0.370	0.589			2.149	0.370	0.637		
Fe5–S4B	2.277	2.120	0.370	0.654			2.149	0.370	0.708		
Fe5–SG	2.355	2.120	0.370	0.530	2.193	0.193	2.149	0.370	0.573	2.372	-0.628
Fe6–S1	2.455	2.120	0.370	0.404			2.149	0.370	0.437		
Fe6–S2B	2.346	2.120	0.370	0.543			2.149	0.370	0.587		
Fe6–S3B	2.333	2.120	0.370	0.562			2.149	0.370	0.608		
Fe6–SG	2.325	2.120	0.370	0.575	2.084	0.084	2.149	0.370	0.621	2.254	-0.746
Fe7–S2B	2.364	2.120	0.370	0.517			2.149	0.370	0.559		
Fe7–S3B	2.329	2.120	0.370	0.568			2.149	0.370	0.615		
Fe7–S4B	2.316	2.120	0.370	0.589			2.149	0.370	0.637		
Fe7–SG	2.322	2.120	0.370	0.579	2.254	0.254	2.149	0.370	0.627	2.437	-0.563
Fe8–S1	2.451	2.120	0.370	0.409			2.149	0.370	0.442		
Fe8–S3B	2.311	2.120	0.370	0.597			2.149	0.370	0.645		
Fe8–S4B	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe8–SG	2.288	2.120	0.370	0.635	2.293	0.293	2.149	0.370	0.687	2.480	-0.520
					18.198					19.682	

Table S33 The adopted bond valence analyses for irons in P-cluster [1] from MoFe protein 1M34 which was reported as P^N at 2.3 Å resolution.

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	2.312	2.120	0.370	0.595			2.149	0.370	0.644		
Fe1–S2A	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe1–S3A	2.307	2.120	0.370	0.603			2.149	0.370	0.652		
Fe1–SG	2.386	2.120	0.370	0.487	2.326	0.326	2.149	0.370	0.527	2.516	-0.484
Fe2–S1	2.364	2.120	0.370	0.517			2.149	0.370	0.559		
Fe2–S2A	2.314	2.120	0.370	0.592			2.149	0.370	0.640		
Fe2–S4A	2.283	2.120	0.370	0.644			2.149	0.370	0.696		
Fe2–SG	2.232	2.120	0.370	0.739	2.492	0.492	2.149	0.370	0.799	2.695	-0.305
Fe3–S2A	2.304	2.120	0.370	0.608			2.149	0.370	0.658		
Fe3–S3A	2.248	2.120	0.370	0.708			2.149	0.370	0.765		
Fe3–S4A	2.339	2.120	0.370	0.553			2.149	0.370	0.598		
Fe3–SG	2.302	2.120	0.370	0.611	2.480	0.480	2.149	0.370	0.661	2.683	-0.317
Fe4–S1	2.292	2.120	0.370	0.628			2.149	0.370	0.679		
Fe4–S3A	2.330	2.120	0.370	0.567			2.149	0.370	0.613		
Fe4–S4A	2.267	2.120	0.370	0.672			2.149	0.370	0.727		

Fe4–SG	2.310	2.120	0.370	0.598	2.466	0.466	2.149	0.370	0.647	2.667	-0.333
Fe5–S1	2.499	2.120	0.370	0.359			2.149	0.370	0.388		
Fe5–S2B	2.294	2.120	0.370	0.625			2.149	0.370	0.676		
Fe5–S4B	2.299	2.120	0.370	0.616			2.149	0.370	0.667		
Fe5–SG	2.241	2.120	0.370	0.721	2.321	0.321	2.149	0.370	0.780	2.511	-0.489
Fe6–S1	2.849	2.120	0.370	0.139			2.149	0.370	0.151		
Fe6–S2B	2.282	2.120	0.370	0.645			2.149	0.370	0.698		
Fe6–S3B	2.290	2.120	0.370	0.632			2.149	0.370	0.683		
Fe6–SG	2.326	2.120	0.370	0.573	1.990	-0.010	2.149	0.370	0.620	2.152	-0.848
Fe7–S2B	2.312	2.120	0.370	0.595			2.149	0.370	0.644		
Fe7–S3B	2.269	2.120	0.370	0.669			2.149	0.370	0.723		
Fe7–S4B	2.342	2.120	0.370	0.549			2.149	0.370	0.594		
Fe7–SG	2.332	2.120	0.370	0.564	2.376	0.376	2.149	0.370	0.610	2.570	-0.430
Fe8–S1	2.359	2.120	0.370	0.524			2.149	0.370	0.567		
Fe8–S3B	2.319	2.120	0.370	0.584			2.149	0.370	0.632		
Fe8–S4B	2.265	2.120	0.370	0.676			2.149	0.370	0.731		
Fe8–SG	2.254	2.120	0.370	0.696	2.480	0.480	2.149	0.370	0.753	2.682	-0.318
					18.931					20.474	

Table S34 The adopted bond valence analyses for irons in P-cluster [2] from MoFe protein 1M34 which was reported as P^N at 2.3 Å resolution.

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	2.317	2.120	0.370	0.587			2.149	0.370	0.635		
Fe1–S2A	2.251	2.120	0.370	0.702			2.149	0.370	0.759		
Fe1–S3A	2.312	2.120	0.370	0.595			2.149	0.370	0.644		
Fe1–SG	2.295	2.120	0.370	0.623	2.507	0.507	2.149	0.370	0.674	2.712	-0.288
Fe2–S1	2.344	2.120	0.370	0.546			2.149	0.370	0.590		
Fe2–S2A	2.313	2.120	0.370	0.594			2.149	0.370	0.642		
Fe2–S4A	2.306	2.120	0.370	0.605			2.149	0.370	0.654		
Fe2–SG	2.209	2.120	0.370	0.786	2.531	0.531	2.149	0.370	0.850	2.737	-0.263
Fe3–S2A	2.302	2.120	0.370	0.611			2.149	0.370	0.661		
Fe3–S3A	2.268	2.120	0.370	0.670			2.149	0.370	0.725		
Fe3–S4A	2.330	2.120	0.370	0.567			2.149	0.370	0.613		
Fe3–SG	2.230	2.120	0.370	0.743	2.592	0.592	2.149	0.370	0.803	2.803	-0.197
Fe4–S1	2.315	2.120	0.370	0.590			2.149	0.370	0.638		
Fe4–S3A	2.311	2.120	0.370	0.597			2.149	0.370	0.645		
Fe4–S4A	2.263	2.120	0.370	0.679			2.149	0.370	0.735		

Fe4–SG	2.103	2.120	0.370	1.047	2.914	0.914	2.149	0.370	1.132	3.151	0.151
Fe5–S1	2.570	2.120	0.370	0.296			2.149	0.370	0.321		
Fe5–S2B	2.281	2.120	0.370	0.647			2.149	0.370	0.700		
Fe5–S4B	2.256	2.120	0.370	0.692			2.149	0.370	0.749		
Fe5–SG	2.258	2.120	0.370	0.689	2.325	0.325	2.149	0.370	0.745	2.514	-0.486
Fe6–S1	2.930	2.120	0.370	0.112			2.149	0.370	0.121		
Fe6–S2B	2.306	2.120	0.370	0.605			2.149	0.370	0.654		
Fe6–S3B	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe6–SG	2.399	2.120	0.370	0.470	1.840	-0.160	2.149	0.370	0.509	1.990	-1.010
Fe7–S2B	2.296	2.120	0.370	0.621			2.149	0.370	0.672		
Fe7–S3B	2.298	2.120	0.370	0.618			2.149	0.370	0.669		
Fe7–S4B	2.316	2.120	0.370	0.589			2.149	0.370	0.637		
Fe7–SG	2.303	2.120	0.370	0.610	2.438	0.438	2.149	0.370	0.660	2.637	-0.363
Fe8–S1	2.498	2.120	0.370	0.360			2.149	0.370	0.389		
Fe8–S3B	2.289	2.120	0.370	0.633			2.149	0.370	0.685		
Fe8–S4B	2.297	2.120	0.370	0.620			2.149	0.370	0.670		
Fe8–SG	2.247	2.120	0.370	0.709	2.323	0.323	2.149	0.370	0.767	2.512	-0.488
					19.468					21.055	

Table S35 The adopted bond valence analyses for irons in P-cluster [3] from MoFe protein 1M34 which was reported as P^N at 2.3 Å resolution.

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	2.324	2.120	0.370	0.576			2.149	0.370	0.623		
Fe1–S2A	2.296	2.120	0.370	0.621			2.149	0.370	0.672		
Fe1–S3A	2.221	2.120	0.370	0.761			2.149	0.370	0.823		
Fe1–SG	2.311	2.120	0.370	0.597	2.556	0.556	2.149	0.370	0.645	2.764	-0.236
Fe2–S1	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe2–S2A	2.305	2.120	0.370	0.607			2.149	0.370	0.656		
Fe2–S4A	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe2–SG	2.274	2.120	0.370	0.660	2.564	0.564	2.149	0.370	0.713	2.773	-0.227
Fe3–S2A	2.294	2.120	0.370	0.625			2.149	0.370	0.676		
Fe3–S3A	2.256	2.120	0.370	0.692			2.149	0.370	0.749		
Fe3–S4A	2.317	2.120	0.370	0.587			2.149	0.370	0.635		
Fe3–SG	2.267	2.120	0.370	0.672	2.577	0.577	2.149	0.370	0.727	2.787	-0.213
Fe4–S1	2.347	2.120	0.370	0.541			2.149	0.370	0.586		
Fe4–S3A	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe4–S4A	2.251	2.120	0.370	0.702			2.149	0.370	0.759		

Fe4–SG	2.226	2.120	0.370	0.751	2.656	0.656	2.149	0.370	0.812	2.872	-0.128
Fe6–S1	2.838	2.120	0.370	0.144			2.149	0.370	0.258		
Fe6–S2B	2.284	2.120	0.370	0.642			2.149	0.370	0.685		
Fe6–S3B	2.268	2.120	0.370	0.670			2.149	0.370	0.751		
Fe6–SG	2.266	2.120	0.370	0.674	2.130	0.130	2.149	0.370	0.635	2.329	-0.671
Fe6–S1	2.838	2.120	0.370	0.144			2.149	0.370	0.155		
Fe6–S2B	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe6–S3B	2.268	2.120	0.370	0.670			2.149	0.370	0.725		
Fe6–SG	2.266	2.120	0.370	0.674	2.130	0.130	2.149	0.370	0.729	2.304	-0.696
Fe7–S2B	2.269	2.120	0.370	0.669			2.149	0.370	0.723		
Fe7–S3B	2.282	2.120	0.370	0.645			2.149	0.370	0.698		
Fe7–S4B	2.259	2.120	0.370	0.687			2.149	0.370	0.743		
Fe7–SG	2.295	2.120	0.370	0.623	2.624	0.624	2.149	0.370	0.674	2.838	-0.162
Fe8–S1	2.607	2.120	0.370	0.268			2.149	0.370	0.290		
Fe8–S3B	2.326	2.120	0.370	0.573			2.149	0.370	0.620		
Fe8–S4B	2.307	2.120	0.370	0.603			2.149	0.370	0.652		
Fe8–SG	2.241	2.120	0.370	0.721	2.166	0.166	2.149	0.370	0.780	2.342	-0.658
					19.425					21.008	

Table S36 The adopted bond valence analyses for irons in P-cluster [4] from MoFe protein 1M34 which was reported as P^N at 2.3 Å resolution.

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	2.265	2.120	0.370	0.676			2.149	0.370	0.731		
Fe1–S2A	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe1–S3A	2.280	2.120	0.370	0.649			2.149	0.370	0.702		
Fe1–SG	2.307	2.120	0.370	0.603	2.589	0.589	2.149	0.370	0.652	2.800	-0.200
Fe2–S1	2.272	2.120	0.370	0.663			2.149	0.370	0.717		
Fe2–S2A	2.267	2.120	0.370	0.672			2.149	0.370	0.727		
Fe2–S4A	2.276	2.120	0.370	0.656			2.149	0.370	0.709		
Fe2–SG	2.277	2.120	0.370	0.654	2.645	0.645	2.149	0.370	0.708	2.861	-0.139
Fe3–S2A	2.292	2.120	0.370	0.628			2.149	0.370	0.679		
Fe3–S3A	2.250	2.120	0.370	0.704			2.149	0.370	0.761		
Fe3–S4A	2.291	2.120	0.370	0.630			2.149	0.370	0.681		
Fe3–SG	2.288	2.120	0.370	0.635	2.597	0.597	2.149	0.370	0.687	2.809	-0.191
Fe4–S1	2.324	2.120	0.370	0.576			2.149	0.370	0.623		
Fe4–S3A	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe4–S4A	2.265	2.120	0.370	0.676			2.149	0.370	0.731		

Fe4–SG	2.253	2.120	0.370	0.698	2.590	0.590	2.149	0.370	0.755	2.801	-0.199
Fe5–S1	2.680	2.120	0.370	0.220			2.149	0.370	0.238		
Fe5–S2B	2.282	2.120	0.370	0.645			2.149	0.370	0.698		
Fe5–S4B	2.258	2.120	0.370	0.689			2.149	0.370	0.745		
Fe5–SG	2.305	2.120	0.370	0.607	2.161	0.161	2.149	0.370	0.656	2.337	-0.663
Fe6–S1	2.947	2.120	0.370	0.107			2.149	0.370	0.116		
Fe6–S2B	2.290	2.120	0.370	0.632			2.149	0.370	0.683		
Fe6–S3B	2.312	2.120	0.370	0.595			2.149	0.370	0.644		
Fe6–SG	2.273	2.120	0.370	0.661	1.995	-0.005	2.149	0.370	0.715	2.158	-0.842
Fe7–S2B	2.302	2.120	0.370	0.611			2.149	0.370	0.661		
Fe7–S3B	2.309	2.120	0.370	0.600			2.149	0.370	0.649		
Fe7–S4B	2.299	2.120	0.370	0.616			2.149	0.370	0.667		
Fe7–SG	2.309	2.120	0.370	0.600	2.428	0.428	2.149	0.370	0.649	2.626	-0.374
Fe8–S1	2.521	2.120	0.370	0.338			2.149	0.370	0.366		
Fe8–S3B	2.290	2.120	0.370	0.632			2.149	0.370	0.683		
Fe8–S4B	2.281	2.120	0.370	0.647			2.149	0.370	0.700		
Fe8–SG	2.252	2.120	0.370	0.700	2.317	0.317	2.149	0.370	0.757	2.506	-0.494
					19.323					20.898	

Table S37 The adopted bond valence analyses for irons in P-cluster [1] from MoFe protein 1QGU which was reported as P^N at 1.6 Å resolution.

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	2.403	2.120	0.370	0.465			2.149	0.370	0.503		
Fe1–S2A	2.315	2.120	0.370	0.590			2.149	0.370	0.638		
Fe1–S3A	2.270	2.120	0.370	0.667			2.149	0.370	0.721		
Fe1–SG	2.399	2.120	0.370	0.470	2.193	0.193	2.149	0.370	0.509	2.372	-0.628
Fe2–S1	2.490	2.120	0.370	0.368			2.149	0.370	0.398		
Fe2–S2A	2.301	2.120	0.370	0.613			2.149	0.370	0.663		
Fe2–S4A	2.274	2.120	0.370	0.660			2.149	0.370	0.713		
Fe2–SG	2.374	2.120	0.370	0.503	2.144	0.144	2.149	0.370	0.544	2.319	-0.681
Fe3–S2A	2.323	2.120	0.370	0.578			2.149	0.370	0.625		
Fe3–S3A	2.380	2.120	0.370	0.495			2.149	0.370	0.536		
Fe3–S4A	2.288	2.120	0.370	0.635			2.149	0.370	0.687		
Fe3–SG	2.378	2.120	0.370	0.498	2.206	0.206	2.149	0.370	0.539	2.386	-0.614
Fe4–S1	2.391	2.120	0.370	0.481			2.149	0.370	0.520		
Fe4–S3A	2.237	2.120	0.370	0.729			2.149	0.370	0.788		
Fe4–S4A	2.273	2.120	0.370	0.661			2.149	0.370	0.715		

Fe4–SG	2.426	2.120	0.370	0.437	2.308	0.308	2.149	0.370	0.473	2.497	-0.503
Fe5–S1	2.426	2.120	0.370	0.437			2.149	0.370	0.473		
Fe5–S2B	2.318	2.120	0.370	0.586			2.149	0.370	0.633		
Fe5–S4B	2.253	2.120	0.370	0.698			2.149	0.370	0.755		
Fe5–SG	2.457	2.120	0.370	0.402	2.123	0.123	2.149	0.370	0.435	2.296	-0.704
Fe6–S1	2.504	2.120	0.370	0.354			2.149	0.370	0.383		
Fe6–S2B	2.316	2.120	0.370	0.589			2.149	0.370	0.637		
Fe6–S3B	2.357	2.120	0.370	0.527			2.149	0.370	0.570		
Fe6–SG	2.316	2.120	0.370	0.589	2.059	0.059	2.149	0.370	0.637	2.227	-0.773
Fe7–S2B	2.361	2.120	0.370	0.521			2.149	0.370	0.564		
Fe7–S3B	2.335	2.120	0.370	0.559			2.149	0.370	0.605		
Fe7–S4B	2.375	2.120	0.370	0.502			2.149	0.370	0.543		
Fe7–SG	2.357	2.120	0.370	0.527	2.110	0.110	2.149	0.370	0.570	2.282	-0.718
Fe8–S1	2.485	2.120	0.370	0.373			2.149	0.370	0.403		
Fe8–S3B	2.386	2.120	0.370	0.487			2.149	0.370	0.527		
Fe8–S4B	2.229	2.120	0.370	0.745			2.149	0.370	0.806		
Fe8–SG	2.311	2.120	0.370	0.597	2.202	0.202	2.149	0.370	0.645	2.381	-0.619
					17.344					18.759	

Table S38 The adopted bond valence analyses for irons in P-cluster [2] from MoFe protein 1QGU which was reported as P^N at 1.6 Å resolution.

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	2.432	2.120	0.370	0.430			2.149	0.370	0.465		
Fe1–S2A	2.373	2.120	0.370	0.505			2.149	0.370	0.546		
Fe1–S3A	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe1–SG	2.387	2.120	0.370	0.486	2.061	0.061	2.149	0.370	0.526	2.229	-0.771
Fe2–S1	2.534	2.120	0.370	0.327			2.149	0.370	0.353		
Fe2–S2A	2.319	2.120	0.370	0.584			2.149	0.370	0.632		
Fe2–S4A	2.288	2.120	0.370	0.635			2.149	0.370	0.687		
Fe2–SG	2.342	2.120	0.370	0.549	2.095	0.095	2.149	0.370	0.594	2.265	-0.735
Fe3–S2A	2.309	2.120	0.370	0.600			2.149	0.370	0.649		
Fe3–S3A	2.366	2.120	0.370	0.514			2.149	0.370	0.556		
Fe3–S4A	2.279	2.120	0.370	0.651			2.149	0.370	0.704		
Fe3–SG	2.406	2.120	0.370	0.462	2.227	0.227	2.149	0.370	0.499	2.408	-0.592
Fe4–S1	2.392	2.120	0.370	0.479			2.149	0.370	0.519		
Fe4–S3A	2.269	2.120	0.370	0.669			2.149	0.370	0.723		
Fe4–S4A	2.290	2.120	0.370	0.632			2.149	0.370	0.683		

Fe4–SG	2.447	2.120	0.370	0.413	2.193	0.193	2.149	0.370	0.447	2.372	-0.628
Fe5–S1	2.401	2.120	0.370	0.468			2.149	0.370	0.506		
Fe5–S2B	2.271	2.120	0.370	0.665			2.149	0.370	0.719		
Fe5–S4B	2.302	2.120	0.370	0.611			2.149	0.370	0.661		
Fe5–SG	2.490	2.120	0.370	0.368	2.112	0.112	2.149	0.370	0.398	2.284	-0.716
Fe6–S1	2.443	2.120	0.370	0.418			2.149	0.370	0.452		
Fe6–S2B	2.308	2.120	0.370	0.602			2.149	0.370	0.651		
Fe6–S3B	2.362	2.120	0.370	0.520			2.149	0.370	0.562		
Fe6–SG	2.344	2.120	0.370	0.546	2.085	0.085	2.149	0.370	0.590	2.255	-0.745
Fe7–S2B	2.379	2.120	0.370	0.497			2.149	0.370	0.537		
Fe7–S3B	2.290	2.120	0.370	0.632			2.149	0.370	0.683		
Fe7–S4B	2.350	2.120	0.370	0.537			2.149	0.370	0.581		
Fe7–SG	2.361	2.120	0.370	0.521	2.187	0.187	2.149	0.370	0.564	2.365	-0.635
Fe8–S1	2.501	2.120	0.370	0.357			2.149	0.370	0.386		
Fe8–S3B	2.293	2.120	0.370	0.627			2.149	0.370	0.678		
Fe8–S4B	2.235	2.120	0.370	0.733			2.149	0.370	0.793		
Fe8–SG	2.327	2.120	0.370	0.572	2.288	0.288	2.149	0.370	0.618	2.475	-0.525
					17.247					18.653	

Table S39 The adopted bond valence analyses for irons in P-cluster [1] from MoFe protein 2AFH which was reported as P^N at 2.1 Å resolution.

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	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe1–S2A	2.253	2.120	0.370	0.698			2.149	0.370	0.755		
Fe1–S3A	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe1–SG	2.299	2.120	0.370	0.616	2.595	0.595	2.149	0.370	0.667	2.807	-0.193
Fe2–S1	2.667	2.120	0.370	0.228			2.149	0.370	0.247		
Fe2–S2A	2.304	2.120	0.370	0.608			2.149	0.370	0.658		
Fe2–S4A	2.286	2.120	0.370	0.638			2.149	0.370	0.691		
Fe2–SG	2.328	2.120	0.370	0.570	2.045	0.045	2.149	0.370	0.616	2.211	-0.789
Fe3–S2A	2.288	2.120	0.370	0.635			2.149	0.370	0.687		
Fe3–S3A	2.267	2.120	0.370	0.672			2.149	0.370	0.727		
Fe3–S4A	2.277	2.120	0.370	0.654			2.149	0.370	0.708		
Fe3–SG	2.264	2.120	0.370	0.678	2.639	0.639	2.149	0.370	0.733	2.854	-0.146
Fe4–S1	2.142	2.120	0.370	0.942			2.149	0.370	1.019		
Fe4–S3A	2.240	2.120	0.370	0.723			2.149	0.370	0.782		
Fe4–S4A	2.258	2.120	0.370	0.689			2.149	0.370	0.745		

Fe4–SG	2.275	2.120	0.370	0.658	3.012	1.012	2.149	0.370	0.711	3.257	0.257
Fe5–S1	2.107	2.120	0.370	1.036			2.149	0.370	1.120		
Fe5–S2B	2.244	2.120	0.370	0.715			2.149	0.370	0.774		
Fe5–S4B	2.264	2.120	0.370	0.678			2.149	0.370	0.733		
Fe5–SG	2.300	2.120	0.370	0.615	3.043	1.043	2.149	0.370	0.665	3.292	0.292
Fe6–S1	2.600	2.120	0.370	0.273			2.149	0.370	0.296		
Fe6–S2B	2.291	2.120	0.370	0.630			2.149	0.370	0.681		
Fe6–S3B	2.269	2.120	0.370	0.669			2.149	0.370	0.723		
Fe6–SG	2.311	2.120	0.370	0.597	2.168	0.168	2.149	0.370	0.645	2.345	-0.655
Fe7–S2B	2.300	2.120	0.370	0.615			2.149	0.370	0.665		
Fe7–S3B	2.303	2.120	0.370	0.610			2.149	0.370	0.660		
Fe7–S4B	2.271	2.120	0.370	0.665			2.149	0.370	0.719		
Fe7–SG	2.350	2.120	0.370	0.537	2.427	0.427	2.149	0.370	0.581	2.624	-0.376
Fe8–S1	2.228	2.120	0.370	0.747			2.149	0.370	0.808		
Fe8–S3B	2.225	2.120	0.370	0.753			2.149	0.370	0.814		
Fe8–S4B	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe8–SG	2.235	2.120	0.370	0.733	2.894	0.894	2.149	0.370	0.793	3.130	0.130
					20.823					22.520	

Table S40 The adopted bond valence analyses for irons in P-cluster [2] from MoFe protein 2AFH which was reported as P^N at 2.1 Å resolution.

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	2.124	2.120	0.370	0.989			2.149	0.370	1.070		
Fe1–S2A	2.265	2.120	0.370	0.676			2.149	0.370	0.731		
Fe1–S3A	2.250	2.120	0.370	0.704			2.149	0.370	0.761		
Fe1–SG	2.268	2.120	0.370	0.670	3.039	1.039	2.149	0.370	0.725	3.287	0.287
Fe2–S1	2.686	2.120	0.370	0.217			2.149	0.370	0.234		
Fe2–S2A	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe2–S4A	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe2–SG	2.338	2.120	0.370	0.555	2.061	0.061	2.149	0.370	0.600	2.229	-0.771
Fe3–S2A	2.266	2.120	0.370	0.674			2.149	0.370	0.729		
Fe3–S3A	2.260	2.120	0.370	0.685			2.149	0.370	0.741		
Fe3–S4A	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe3–SG	2.242	2.120	0.370	0.719	2.720	0.720	2.149	0.370	0.778	2.942	-0.058
Fe4–S1	2.127	2.120	0.370	0.981			2.149	0.370	1.061		
Fe4–S3A	2.258	2.120	0.370	0.689			2.149	0.370	0.745		
Fe4–S4A	2.243	2.120	0.370	0.717			2.149	0.370	0.776		

Fe4–SG	2.263	2.120	0.370	0.679	3.067	1.067	2.149	0.370	0.735	3.317	0.317
Fe5–S1	2.155	2.120	0.370	0.910			2.149	0.370	0.984		
Fe5–S2B	2.237	2.120	0.370	0.729			2.149	0.370	0.788		
Fe5–S4B	2.281	2.120	0.370	0.647			2.149	0.370	0.700		
Fe5–SG	2.278	2.120	0.370	0.652	2.938	0.938	2.149	0.370	0.706	3.178	0.178
Fe6–S1	2.634	2.120	0.370	0.249			2.149	0.370	0.270		
Fe6–S2B	2.296	2.120	0.370	0.621			2.149	0.370	0.672		
Fe6–S3B	2.295	2.120	0.370	0.623			2.149	0.370	0.674		
Fe6–SG	2.328	2.120	0.370	0.570	2.064	0.064	2.149	0.370	0.616	2.232	-0.768
Fe7–S2B	2.309	2.120	0.370	0.600			2.149	0.370	0.649		
Fe7–S3B	2.319	2.120	0.370	0.584			2.149	0.370	0.632		
Fe7–S4B	2.263	2.120	0.370	0.679			2.149	0.370	0.735		
Fe7–SG	2.326	2.120	0.370	0.573	2.437	0.437	2.149	0.370	0.620	2.635	-0.365
Fe8–S1	2.169	2.120	0.370	0.876			2.149	0.370	0.947		
Fe8–S3B	2.244	2.120	0.370	0.715			2.149	0.370	0.774		
Fe8–S4B	2.264	2.120	0.370	0.678			2.149	0.370	0.733		
Fe8–SG	2.205	2.120	0.370	0.795	3.064	1.064	2.149	0.370	0.860	3.313	0.313
					21.388					23.132	

Table S41 The adopted bond valence analyses for irons in P-cluster [1] from MoFe protein 3MIN which was reported as P^N at 2.03 Å resolution.

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	2.259	2.120	0.370	0.687			2.149	0.370	0.743		
Fe1–S2A	2.154	2.120	0.370	0.912			2.149	0.370	0.987		
Fe1–S3A	2.302	2.120	0.370	0.611			2.149	0.370	0.661		
Fe1–SG	2.193	2.120	0.370	0.821	3.031	1.031	2.149	0.370	0.888	3.279	0.279
Fe2–S1	2.343	2.120	0.370	0.547			2.149	0.370	0.592		
Fe2–S2A	2.226	2.120	0.370	0.751			2.149	0.370	0.812		
Fe2–S4A	2.195	2.120	0.370	0.817			2.149	0.370	0.883		
Fe2–SG	2.440	2.120	0.370	0.421	2.536	0.536	2.149	0.370	0.455	2.743	-0.257
Fe3–S2A	2.233	2.120	0.370	0.737			2.149	0.370	0.797		
Fe3–S3A	2.298	2.120	0.370	0.618			2.149	0.370	0.669		
Fe3–S4A	2.264	2.120	0.370	0.678			2.149	0.370	0.733		
Fe3–SG	2.204	2.120	0.370	0.797	2.829	0.829	2.149	0.370	0.862	3.060	0.060
Fe4–S1	2.225	2.120	0.370	0.753			2.149	0.370	0.814		
Fe4–S3A	2.211	2.120	0.370	0.782			2.149	0.370	0.846		
Fe4–S4A	2.157	2.120	0.370	0.905			2.149	0.370	0.979		

Fe4–SG	2.209	2.120	0.370	0.786	3.226	1.226	2.149	0.370	0.850	3.489	0.489
Fe5–S1	2.427	2.120	0.370	0.436			2.149	0.370	0.472		
Fe5–S2B	2.202	2.120	0.370	0.801			2.149	0.370	0.867		
Fe5–S4B	2.135	2.120	0.370	0.960			2.149	0.370	1.039		
Fe5–SG	2.331	2.120	0.370	0.565	2.763	0.763	2.149	0.370	0.611	2.988	-0.012
Fe6–S1	2.916	2.120	0.370	0.116			2.149	0.370	0.126		
Fe6–S2B	2.263	2.120	0.370	0.679			2.149	0.370	0.735		
Fe6–S3B	2.206	2.120	0.370	0.793			2.149	0.370	0.857		
Fe6–SG	2.288	2.120	0.370	0.635	2.223	0.223	2.149	0.370	0.687	2.405	-0.595
Fe7–S2B	2.156	2.120	0.370	0.907			2.149	0.370	0.981		
Fe7–S3B	2.269	2.120	0.370	0.669			2.149	0.370	0.723		
Fe7–S4B	2.385	2.120	0.370	0.489			2.149	0.370	0.528		
Fe7–SG	2.358	2.120	0.370	0.526	2.590	0.590	2.149	0.370	0.568	2.801	-0.199
Fe8–S1	2.445	2.120	0.370	0.415			2.149	0.370	0.449		
Fe8–S3B	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe8–S4B	2.289	2.120	0.370	0.633			2.149	0.370	0.685		
Fe8–SG	2.306	2.120	0.370	0.605	2.306	0.306	2.149	0.370	0.654	2.494	-0.506
					21.505					23.259	

Table S42 The adopted bond valence analyses for irons in P-cluster [2] from MoFe protein 3MIN which was reported as P^N at 2.03 Å resolution.

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	2.380	2.120	0.370	0.495			2.149	0.370	0.536		
Fe1–S2A	2.207	2.120	0.370	0.790			2.149	0.370	0.855		
Fe1–S3A	2.197	2.120	0.370	0.812			2.149	0.370	0.878		
Fe1–SG	2.326	2.120	0.370	0.573	2.671	0.671	2.149	0.370	0.620	2.889	-0.111
Fe2–S1	2.500	2.120	0.370	0.358			2.149	0.370	0.387		
Fe2–S2A	2.210	2.120	0.370	0.784			2.149	0.370	0.848		
Fe2–S4A	2.314	2.120	0.370	0.592			2.149	0.370	0.640		
Fe2–SG	2.315	2.120	0.370	0.590	2.324	0.324	2.149	0.370	0.638	2.514	-0.486
Fe3–S2A	2.212	2.120	0.370	0.780			2.149	0.370	0.843		
Fe3–S3A	2.215	2.120	0.370	0.774			2.149	0.370	0.837		
Fe3–S4A	2.398	2.120	0.370	0.472			2.149	0.370	0.510		
Fe3–SG	2.213	2.120	0.370	0.778	2.803	0.803	2.149	0.370	0.841	3.031	0.031
Fe4–S1	2.417	2.120	0.370	0.448			2.149	0.370	0.485		
Fe4–S3A	2.246	2.120	0.370	0.711			2.149	0.370	0.769		
Fe4–S4A	2.221	2.120	0.370	0.761			2.149	0.370	0.823		

Fe4–SG	2.267	2.120	0.370	0.672	2.593	0.593	2.149	0.370	0.727	2.804	-0.196
Fe5–S1	2.356	2.120	0.370	0.528			2.149	0.370	0.572		
Fe5–S2B	2.322	2.120	0.370	0.579			2.149	0.370	0.627		
Fe5–S4B	2.252	2.120	0.370	0.700			2.149	0.370	0.757		
Fe5–SG	2.314	2.120	0.370	0.592	2.400	0.400	2.149	0.370	0.640	2.595	-0.405
Fe6–S1	2.603	2.120	0.370	0.271			2.149	0.370	0.293		
Fe6–S2B	2.280	2.120	0.370	0.649			2.149	0.370	0.702		
Fe6–S3B	2.327	2.120	0.370	0.572			2.149	0.370	0.618		
Fe6–SG	2.355	2.120	0.370	0.530	2.021	0.021	2.149	0.370	0.573	2.186	-0.814
Fe7–S2B	2.297	2.120	0.370	0.620			2.149	0.370	0.670		
Fe7–S3B	2.262	2.120	0.370	0.681			2.149	0.370	0.737		
Fe7–S4B	2.300	2.120	0.370	0.615			2.149	0.370	0.665		
Fe7–SG	2.323	2.120	0.370	0.578	2.494	0.494	2.149	0.370	0.625	2.697	-0.303
Fe8–S1	2.306	2.120	0.370	0.605			2.149	0.370	0.654		
Fe8–S3B	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe8–S4B	2.330	2.120	0.370	0.567			2.149	0.370	0.613		
Fe8–SG	2.246	2.120	0.370	0.711	2.536	0.536	2.149	0.370	0.769	2.742	-0.258
					19.841					21.459	

Table S43 The adopted bond valence analyses for irons in P^N [1] from MoFe protein 3U7Q which was reported as superposition of $P^N/^{2+}$ at 1.0 Å resolution.

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	2.389	2.120	0.370	0.483			2.149	0.370	0.523		
Fe1–S2A	2.308	2.120	0.370	0.602			2.149	0.370	0.651		
Fe1–S4A	2.311	2.120	0.370	0.597			2.149	0.370	0.645		
Fe1–SG	2.323	2.120	0.370	0.578	2.259	0.259	2.149	0.370	0.625	2.444	-0.556
Fe2–S1	2.484	2.120	0.370	0.374			2.149	0.370	0.404		
Fe2–S2A	2.296	2.120	0.370	0.621			2.149	0.370	0.672		
Fe2–S3A	2.277	2.120	0.370	0.654			2.149	0.370	0.708		
Fe2–SG	2.341	2.120	0.370	0.550	2.200	0.200	2.149	0.370	0.595	2.379	-0.621
Fe3–S2A	2.291	2.120	0.370	0.630			2.149	0.370	0.681		
Fe3–S3A	2.313	2.120	0.370	0.594			2.149	0.370	0.642		
Fe3–S4A	2.265	2.120	0.370	0.676			2.149	0.370	0.731		
Fe3–SG	2.292	2.120	0.370	0.628	2.527	0.527	2.149	0.370	0.679	2.734	-0.266
Fe4–S1	2.366	2.120	0.370	0.514			2.149	0.370	0.556		
Fe4–S3A	2.296	2.120	0.370	0.621			2.149	0.370	0.672		
Fe4–S4A	2.287	2.120	0.370	0.637			2.149	0.370	0.689		

Fe4–SG	2.314	2.120	0.370	0.592	2.365	0.365	2.149	0.370	0.640	2.557	-0.443
Fe5–S1(P^N)	2.568	2.120	0.370	0.298			2.149	0.370	0.322		
Fe5–S2B(P^N)	2.448	2.120	0.370	0.412			2.149	0.370	0.446		
Fe5–S4B(P^N)	2.219	2.120	0.370	0.765			2.149	0.370	0.828		
Fe5–SG(P^N)	2.296	2.120	0.370	0.621	2.097 (P^N)	0.097	2.149	0.370	0.672	2.268 (P^N)	-0.732
Fe6–S1(P^N)	2.558	2.120	0.370	0.306			2.149	0.370	0.331		
Fe6–S2B(P^N)	2.578	2.120	0.370	0.290			2.149	0.370	0.314		
Fe6–S3B(P^N)	2.313	2.120	0.370	0.594			2.149	0.370	0.642		
Fe6–SG(P^N)	2.248	2.120	0.370	0.708	1.897 (P^N)	-0.103	2.149	0.370	0.765	2.052 (P^N)	-0.948
Fe7–S2B	2.309	2.120	0.370	0.600			2.149	0.370	0.649		
Fe7–S3B	2.320	2.120	0.370	0.582			2.149	0.370	0.630		
Fe7–S4B	2.289	2.120	0.370	0.633			2.149	0.370	0.685		
Fe7–SG	2.373	2.120	0.370	0.505	2.320	0.320	2.149	0.370	0.546	2.510	-0.490
Fe8–S1	2.346	2.120	0.370	0.543			2.149	0.370	0.587		
Fe8–S3B	2.283	2.120	0.370	0.644			2.149	0.370	0.696		
Fe8–S4B	2.324	2.120	0.370	0.576			2.149	0.370	0.623		
Fe8–SG	2.313	2.120	0.370	0.594	2.356	0.356	2.149	0.370	0.642	2.548	-0.452
					18.022 (P^N)					19.492 (P^N)	

Table S44 The adopted bond valence analyses for irons in P^N [2] from MoFe protein 3U7Q which was reported as superposition of $P^N/^{2+}$ at 1.0 Å resolution.

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	2.384	2.120	0.370	0.490			2.149	0.370	0.530		
Fe1–S2A	2.307	2.120	0.370	0.603			2.149	0.370	0.652		
Fe1–S4A	2.306	2.120	0.370	0.605			2.149	0.370	0.654		
Fe1–SG	2.319	2.120	0.370	0.584	2.282	0.282	2.149	0.370	0.632	2.468	-0.532
Fe2–S1	2.482	2.120	0.370	0.376			2.149	0.370	0.407		
Fe2–S2A	2.302	2.120	0.370	0.611			2.149	0.370	0.661		
Fe2–S3A	2.279	2.120	0.370	0.651			2.149	0.370	0.704		
Fe2–SG	2.334	2.120	0.370	0.561	2.199	0.199	2.149	0.370	0.607	2.378	-0.622
Fe3–S2A	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe3–S3A	2.321	2.120	0.370	0.581			2.149	0.370	0.628		
Fe3–S4A	2.264	2.120	0.370	0.678			2.149	0.370	0.733		
Fe3–SG	2.287	2.120	0.370	0.637	2.532	0.532	2.149	0.370	0.689	2.738	-0.262
Fe4–S1	2.356	2.120	0.370	0.528			2.149	0.370	0.572		
Fe4–S3A	2.303	2.120	0.370	0.610			2.149	0.370	0.660		
Fe4–S4A	2.287	2.120	0.370	0.637			2.149	0.370	0.689		

Fe4–SG	2.317	2.120	0.370	0.587	2.362	0.362	2.149	0.370	0.635	2.555	-0.445
Fe5–S1(P^N)	2.634	2.120	0.370	0.249			2.149	0.370	0.270		
Fe5–S2B(P^N)	2.444	2.120	0.370	0.417			2.149	0.370	0.451		
Fe5–S4B(P^N)	2.198	2.120	0.370	0.810			2.149	0.370	0.876		
Fe5–SG(P^N)	2.272	2.120	0.370	0.663	2.139 (P^N)	0.139	2.149	0.370	0.717	2.313 (P^N)	-0.687
Fe6–S1(P^N)	2.559	2.120	0.370	0.305			2.149	0.370	0.330		
Fe6–S2B(P^N)	2.551	2.120	0.370	0.312			2.149	0.370	0.337		
Fe6–S3B(P^N)	2.326	2.120	0.370	0.573			2.149	0.370	0.620		
Fe6–SG(P^N)	2.265	2.120	0.370	0.676	1.866 (P^N)	-0.134	2.149	0.370	0.731	2.018 (P^N)	-0.982
Fe7–S2B	2.317	2.120	0.370	0.587			2.149	0.370	0.635		
Fe7–S3B	2.323	2.120	0.370	0.578			2.149	0.370	0.625		
Fe7–S4B	2.292	2.120	0.370	0.628			2.149	0.370	0.679		
Fe7–SG	2.368	2.120	0.370	0.512	2.305	0.305	2.149	0.370	0.553	2.493	-0.507
Fe8–S1	2.357	2.120	0.370	0.527			2.149	0.370	0.570		
Fe8–S3B	2.277	2.120	0.370	0.654			2.149	0.370	0.708		
Fe8–S4B	2.322	2.120	0.370	0.579			2.149	0.370	0.627		
Fe8–SG	2.314	2.120	0.370	0.592	2.352	0.352	2.149	0.370	0.640	2.544	-0.456
					18.037 (P^N)					19.508 (P^N)	

Table S45 The adopted bond valence analyses for irons in P-cluster [1] from MoFe protein 4TKU which was reported as P^N at 1.43 Å resolution.

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	2.468	2.12	0.37	0.390			2.149	0.37	0.422		
Fe1–S2A	2.291	2.12	0.37	0.630			2.149	0.37	0.681		
Fe1–S3A	2.260	2.12	0.37	0.685			2.149	0.37	0.741		
Fe1–SG	2.343	2.12	0.37	0.547	2.253	0.253	2.149	0.37	0.592	2.436	-0.564
Fe2–S1	2.466	2.12	0.37	0.393			2.149	0.37	0.425		
Fe2–S2A	2.284	2.12	0.37	0.642			2.149	0.37	0.694		
Fe2–S4A	2.280	2.12	0.37	0.649			2.149	0.37	0.702		
Fe2–SG	2.342	2.12	0.37	0.549	2.232	0.232	2.149	0.37	0.594	2.414	-0.586
Fe3–S2A	2.290	2.12	0.37	0.632			2.149	0.37	0.683		
Fe3–S3A	2.256	2.12	0.37	0.692			2.149	0.37	0.749		
Fe3–S4A	2.331	2.12	0.37	0.565			2.149	0.37	0.611		
Fe3–SG	2.280	2.12	0.37	0.649	2.538	0.538	2.149	0.37	0.702	2.745	-0.255
Fe4–S1	2.383	2.12	0.37	0.491			2.149	0.37	0.531		
Fe4–S3A	2.262	2.12	0.37	0.681			2.149	0.37	0.737		
Fe4–S4A	2.293	2.12	0.37	0.627			2.149	0.37	0.678		

Fe4–SG	2.315	2.12	0.37	0.590	2.389	0.389	2.149	0.37	0.638	2.584	-0.416
Fe5–S1	2.413	2.12	0.37	0.453			2.149	0.37	0.490		
Fe5–S2B	2.264	2.12	0.37	0.678			2.149	0.37	0.733		
Fe5–S4B	2.317	2.12	0.37	0.587			2.149	0.37	0.635		
Fe5–SG	2.351	2.12	0.37	0.536	2.253	0.253	2.149	0.37	0.579	2.437	-0.563
Fe6–S1	2.465	2.12	0.37	0.394			2.149	0.37	0.426		
Fe6–S2B	2.289	2.12	0.37	0.633			2.149	0.37	0.685		
Fe6–S3B	2.339	2.12	0.37	0.553			2.149	0.37	0.598		
Fe6–SG	2.325	2.12	0.37	0.575	2.155	0.155	2.149	0.37	0.621	2.331	-0.669
Fe7–S2B	2.298	2.12	0.37	0.618			2.149	0.37	0.669		
Fe7–S3B	2.337	2.12	0.37	0.556			2.149	0.37	0.602		
Fe7–S4B	2.332	2.12	0.37	0.564			2.149	0.37	0.610		
Fe7–SG	2.367	2.12	0.37	0.513	2.251	0.251	2.149	0.37	0.555	2.435	-0.565
Fe8–S1	2.406	2.12	0.37	0.462			2.149	0.37	0.499		
Fe8–S3B	2.309	2.12	0.37	0.600			2.149	0.37	0.649		
Fe8–S4B	2.302	2.12	0.37	0.611			2.149	0.37	0.661		
Fe8–SG	2.298	2.12	0.37	0.618	2.291	0.291	2.149	0.37	0.669	2.478	-0.522
					18.363					19.860	

Table S46 The adopted bond valence analyses for irons in P-cluster [2] from MoFe protein 4TKU which was reported as P^N at 1.43 Å resolution.

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	2.468	2.12	0.37	0.404			2.149	0.37	0.437		
Fe1–S2A	2.291	2.12	0.37	0.649			2.149	0.37	0.702		
Fe1–S3A	2.260	2.12	0.37	0.670			2.149	0.37	0.725		
Fe1–SG	2.343	2.12	0.37	0.594	2.253	0.253	2.149	0.37	0.642	2.436	-0.564
Fe2–S1	2.466	2.12	0.37	0.409			2.149	0.37	0.442		
Fe2–S2A	2.284	2.12	0.37	0.621			2.149	0.37	0.672		
Fe2–S4A	2.280	2.12	0.37	0.628			2.149	0.37	0.679		
Fe2–SG	2.342	2.12	0.37	0.586	2.232	0.232	2.149	0.37	0.633	2.414	-0.586
Fe3–S2A	2.290	2.12	0.37	0.623			2.149	0.37	0.674		
Fe3–S3A	2.256	2.12	0.37	0.709			2.149	0.37	0.767		
Fe3–S4A	2.331	2.12	0.37	0.567			2.149	0.37	0.613		
Fe3–SG	2.280	2.12	0.37	0.663	2.538	0.538	2.149	0.37	0.717	2.745	-0.255
Fe4–S1	2.383	2.12	0.37	0.481			2.149	0.37	0.520		
Fe4–S3A	2.262	2.12	0.37	0.678			2.149	0.37	0.733		
Fe4–S4A	2.293	2.12	0.37	0.642			2.149	0.37	0.694		

Fe4–SG	2.315	2.12	0.37	0.572	2.389	0.389	2.149	0.37	0.618	2.584	-0.416
Fe5–S1	2.413	2.12	0.37	0.448			2.149	0.37	0.485		
Fe5–S2B	2.264	2.12	0.37	0.681			2.149	0.37	0.737		
Fe5–S4B	2.317	2.12	0.37	0.594			2.149	0.37	0.642		
Fe5–SG	2.351	2.12	0.37	0.546	2.253	0.253	2.149	0.37	0.590	2.437	-0.563
Fe6–S1	2.465	2.12	0.37	0.384			2.149	0.37	0.415		
Fe6–S2B	2.289	2.12	0.37	0.618			2.149	0.37	0.669		
Fe6–S3B	2.339	2.12	0.37	0.556			2.149	0.37	0.602		
Fe6–SG	2.325	2.12	0.37	0.578	2.155	0.155	2.149	0.37	0.625	2.331	-0.669
Fe7–S2B	2.298	2.12	0.37	0.620			2.149	0.37	0.670		
Fe7–S3B	2.337	2.12	0.37	0.549			2.149	0.37	0.594		
Fe7–S4B	2.332	2.12	0.37	0.558			2.149	0.37	0.603		
Fe7–SG	2.367	2.12	0.37	0.505	2.251	0.251	2.149	0.37	0.546	2.435	-0.565
Fe8–S1	2.406	2.12	0.37	0.485			2.149	0.37	0.524		
Fe8–S3B	2.309	2.12	0.37	0.589			2.149	0.37	0.637		
Fe8–S4B	2.302	2.12	0.37	0.628			2.149	0.37	0.679		
Fe8–SG	2.298	2.12	0.37	0.615	2.291	0.291	2.149	0.37	0.665	2.478	-0.522
					18.363					19.860	

Table S47 The adopted bond valence analyses for irons in P-cluster [1] from MoFe protein 4TKV which was reported as P^N at 1.5 Å resolution.

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	2.421	2.120	0.370	0.443			2.149	0.370	0.479		
Fe1–S2A	2.303	2.120	0.370	0.610			2.149	0.370	0.660		
Fe1–S3A	2.267	2.120	0.370	0.672			2.149	0.370	0.727		
Fe1–SG	2.296	2.120	0.370	0.621	2.347	0.347	2.149	0.370	0.672	2.538	-0.462
Fe2–S1	2.455	2.120	0.370	0.404			2.149	0.370	0.437		
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	2.298	2.120	0.370	0.618	2.314	0.314	2.149	0.370	0.669	2.503	-0.497
Fe3–S2A	2.279	2.120	0.370	0.651			2.149	0.370	0.704		
Fe3–S3A	2.242	2.120	0.370	0.719			2.149	0.370	0.778		
Fe3–S4A	2.336	2.120	0.370	0.558			2.149	0.370	0.603		
Fe3–SG	2.283	2.120	0.370	0.644	2.571	0.571	2.149	0.370	0.696	2.781	-0.219
Fe4–S1	2.379	2.120	0.370	0.497			2.149	0.370	0.537		
Fe4–S3A	2.241	2.120	0.370	0.721			2.149	0.370	0.780		
Fe4–S4A	2.295	2.120	0.370	0.623			2.149	0.370	0.674		

Fe4–SG	2.322	2.120	0.370	0.579	2.420	0.420	2.149	0.370	0.627	2.617	-0.383
Fe5–S1	2.414	2.120	0.370	0.452			2.149	0.370	0.489		
Fe5–S2B	2.234	2.120	0.370	0.735			2.149	0.370	0.795		
Fe5–S4B	2.345	2.120	0.370	0.544			2.149	0.370	0.589		
Fe5–SG	2.312	2.120	0.370	0.595	2.326	0.326	2.149	0.370	0.644	2.516	-0.484
Fe6–S1	2.471	2.120	0.370	0.387			2.149	0.370	0.419		
Fe6–S2B	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe6–S3B	2.312	2.120	0.370	0.595			2.149	0.370	0.644		
Fe6–SG	2.340	2.120	0.370	0.552	2.187	0.187	2.149	0.370	0.597	2.365	-0.635
Fe7–S2B	2.298	2.120	0.370	0.618			2.149	0.370	0.669		
Fe7–S3B	2.326	2.120	0.370	0.573			2.149	0.370	0.620		
Fe7–S4B	2.300	2.120	0.370	0.615			2.149	0.370	0.665		
Fe7–SG	2.370	2.120	0.370	0.509	2.315	0.315	2.149	0.370	0.550	2.504	-0.496
Fe8–S1	2.400	2.120	0.370	0.469			2.149	0.370	0.507		
Fe8–S3B	2.275	2.120	0.370	0.658			2.149	0.370	0.711		
Fe8–S4B	2.276	2.120	0.370	0.656			2.149	0.370	0.709		
Fe8–SG	2.305	2.120	0.370	0.607	2.389	0.389	2.149	0.370	0.656	2.584	-0.416
					18.869					20.408	

Table S48 The adopted bond valence analyses for irons in P-cluster [2] from MoFe protein 4TKV which was reported as P^N at 1.5 Å resolution.

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	2.430	2.120	0.370	0.433			2.149	0.370	0.468		
Fe1–S2A	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe1–S3A	2.263	2.120	0.370	0.679			2.149	0.370	0.735		
Fe1–SG	2.325	2.120	0.370	0.575	2.323	0.323	2.149	0.370	0.621	2.513	-0.487
Fe2–S1	2.431	2.120	0.370	0.431			2.149	0.370	0.467		
Fe2–S2A	2.264	2.120	0.370	0.678			2.149	0.370	0.733		
Fe2–S4A	2.271	2.120	0.370	0.665			2.149	0.370	0.719		
Fe2–SG	2.317	2.120	0.370	0.587	2.361	0.361	2.149	0.370	0.635	2.554	-0.446
Fe3–S2A	2.265	2.120	0.370	0.676			2.149	0.370	0.731		
Fe3–S3A	2.244	2.120	0.370	0.715			2.149	0.370	0.774		
Fe3–S4A	2.313	2.120	0.370	0.594			2.149	0.370	0.642		
Fe3–SG	2.286	2.120	0.370	0.638	2.623	0.623	2.149	0.370	0.691	2.837	-0.163
Fe4–S1	2.382	2.120	0.370	0.493			2.149	0.370	0.533		
Fe4–S3A	2.251	2.120	0.370	0.702			2.149	0.370	0.759		
Fe4–S4A	2.279	2.120	0.370	0.651			2.149	0.370	0.704		

Fe4–SG	2.358	2.120	0.370	0.526	2.371	0.371	2.149	0.370	0.568	2.564	-0.436
Fe5–S1	2.431	2.120	0.370	0.431			2.149	0.370	0.467		
Fe5–S2B	2.247	2.120	0.370	0.709			2.149	0.370	0.767		
Fe5–S4B	2.313	2.120	0.370	0.594			2.149	0.370	0.642		
Fe5–SG	2.322	2.120	0.370	0.579	2.314	0.314	2.149	0.370	0.627	2.502	-0.498
Fe6–S1	2.491	2.120	0.370	0.367			2.149	0.370	0.397		
Fe6–S2B	2.298	2.120	0.370	0.618			2.149	0.370	0.669		
Fe6–S3B	2.341	2.120	0.370	0.550			2.149	0.370	0.595		
Fe6–SG	2.337	2.120	0.370	0.556	2.092	0.092	2.149	0.370	0.602	2.262	-0.738
Fe7–S2B	2.304	2.120	0.370	0.608			2.149	0.370	0.658		
Fe7–S3B	2.337	2.120	0.370	0.556			2.149	0.370	0.602		
Fe7–S4B	2.334	2.120	0.370	0.561			2.149	0.370	0.607		
Fe7–SG	2.358	2.120	0.370	0.526	2.251	0.251	2.149	0.370	0.568	2.434	-0.566
Fe8–S1	2.406	2.120	0.370	0.462			2.149	0.370	0.499		
Fe8–S3B	2.281	2.120	0.370	0.647			2.149	0.370	0.700		
Fe8–S4B	2.290	2.120	0.370	0.632			2.149	0.370	0.683		
Fe8–SG	2.356	2.120	0.370	0.528	2.269	0.269	2.149	0.370	0.572	2.454	-0.546
					18.603					20.120	

Table S49 The adopted bond valence analyses for irons in P^N [1] from MoFe protein 4WES which was reported as superposition of $P^N/^{2+}$ at 1.08 Å resolution.

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	2.373	2.120	0.370	0.505			2.149	0.370	0.546		
Fe1–S2A	2.331	2.120	0.370	0.565			2.149	0.370	0.611		
Fe1–S4A	2.330	2.120	0.370	0.567			2.149	0.370	0.613		
Fe1–SG	2.321	2.120	0.370	0.581	2.218	0.218	2.149	0.370	0.628	2.399	-0.601
Fe2–S1	2.468	2.120	0.370	0.390			2.149	0.370	0.422		
Fe2–S2A	2.301	2.120	0.370	0.613			2.149	0.370	0.663		
Fe2–S3A	2.301	2.120	0.370	0.613			2.149	0.370	0.663		
Fe2–SG	2.363	2.120	0.370	0.519	2.135	0.135	2.149	0.370	0.561	2.309	-0.691
Fe3–S2A	2.319	2.120	0.370	0.584			2.149	0.370	0.632		
Fe3–S3A	2.330	2.120	0.370	0.567			2.149	0.370	0.613		
Fe3–S4A	2.271	2.120	0.370	0.665			2.149	0.370	0.719		
Fe3–SG	2.303	2.120	0.370	0.610	2.426	0.426	2.149	0.370	0.660	2.623	-0.377
Fe4–S1	2.382	2.120	0.370	0.493			2.149	0.370	0.533		
Fe4–S3A	2.318	2.120	0.370	0.586			2.149	0.370	0.633		
Fe4–S4A	2.285	2.120	0.370	0.640			2.149	0.370	0.692		

Fe4–SG	2.338	2.120	0.370	0.555	2.273	0.273	2.149	0.370	0.600	2.458	-0.542
Fe5–S1(P^N)	2.438	2.120	0.370	0.423			2.149	0.370	0.458		
Fe5–S2B(P^N)	2.515	2.120	0.370	0.344			2.149	0.370	0.372		
Fe5–S4B(P^N)	2.251	2.120	0.370	0.702			2.149	0.370	0.759		
Fe5–SG(P^N)	2.321	2.120	0.370	0.581	2.050 (P^N)	0.050	2.149	0.370	0.628	2.217 (P^N)	-0.783
Fe6–S1(P^N)	2.476	2.120	0.370	0.382			2.149	0.370	0.413		
Fe6–S2B(P^N)	2.527	2.120	0.370	0.333			2.149	0.370	0.360		
Fe6–S3B(P^N)	2.386	2.120	0.370	0.487			2.149	0.370	0.527		
Fe6–SG(P^N)	2.302	2.120	0.370	0.611	1.814 (P^N)	-0.186	2.149	0.370	0.661	1.962 (P^N)	-1.038
Fe7–S2B	2.300	2.120	0.370	0.615			2.149	0.370	0.665		
Fe7–S3B	2.317	2.120	0.370	0.587			2.149	0.370	0.635		
Fe7–S4B	2.318	2.120	0.370	0.586			2.149	0.370	0.633		
Fe7–SG	2.322	2.120	0.370	0.579	2.367	0.367	2.149	0.370	0.627	2.560	-0.440
Fe8–S1	2.369	2.120	0.370	0.510			2.149	0.370	0.552		
Fe8–S3B	2.271	2.120	0.370	0.665			2.149	0.370	0.719		
Fe8–S4B	2.325	2.120	0.370	0.575			2.149	0.370	0.621		
Fe8–SG	2.312	2.120	0.370	0.595	2.345	0.345	2.149	0.370	0.644	2.536	-0.464
					17.627 (P^N)					19.064 (P^N)	

Table S50 The adopted bond valence analyses for irons in P^N [2] from MoFe protein 4WES which was reported as superposition of $P^N/^{2+}$ in 1.08 Å resolution.

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	2.385	2.120	0.370	0.489			2.149	0.370	0.528		
Fe1–S2A	2.334	2.120	0.370	0.561			2.149	0.370	0.607		
Fe1–S4A	2.332	2.120	0.370	0.564			2.149	0.370	0.610		
Fe1–SG	2.313	2.120	0.370	0.594	2.207	0.207	2.149	0.370	0.642	2.387	-0.613
Fe2–S1	2.478	2.120	0.370	0.380			2.149	0.370	0.411		
Fe2–S2A	2.294	2.120	0.370	0.625			2.149	0.370	0.676		
Fe2–S3A	2.307	2.120	0.370	0.603			2.149	0.370	0.652		
Fe2–SG	2.357	2.120	0.370	0.527	2.135	0.135	2.149	0.370	0.570	2.309	-0.691
Fe3–S2A	2.320	2.120	0.370	0.582			2.149	0.370	0.630		
Fe3–S3A	2.334	2.120	0.370	0.561			2.149	0.370	0.607		
Fe3–S4A	2.283	2.120	0.370	0.644			2.149	0.370	0.696		
Fe3–SG	2.293	2.120	0.370	0.627	2.413	0.413	2.149	0.370	0.678	2.610	-0.390
Fe4–S1	2.388	2.120	0.370	0.485			2.149	0.370	0.524		
Fe4–S3A	2.314	2.120	0.370	0.592			2.149	0.370	0.640		
Fe4–S4A	2.278	2.120	0.370	0.652			2.149	0.370	0.706		

Fe4–SG	2.343	2.120	0.370	0.547	2.276	0.276	2.149	0.370	0.592	2.462	-0.538
Fe5–S1(P^N)	2.412	2.120	0.370	0.454			2.149	0.370	0.491		
Fe5–S2B(P^N)	2.502	2.120	0.370	0.356			2.149	0.370	0.385		
Fe5–S4B(P^N)	2.251	2.120	0.370	0.702			2.149	0.370	0.759		
Fe5–SG(P^N)	2.330	2.120	0.370	0.567	2.079 (P^N)	0.079	2.149	0.370	0.613	2.249 (P^N)	-0.751
Fe6–S1(P^N)	2.413	2.120	0.370	0.453			2.149	0.370	0.490		
Fe6–S2B(P^N)	2.553	2.120	0.370	0.310			2.149	0.370	0.336		
Fe6–S3B(P^N)	2.383	2.120	0.370	0.491			2.149	0.370	0.531		
Fe6–SG(P^N)	2.291	2.120	0.370	0.630	1.884 (P^N)	-0.116	2.149	0.370	0.681	2.038 (P^N)	-0.962
Fe7–S2B	2.299	2.120	0.370	0.616			2.149	0.370	0.667		
Fe7–S3B	2.317	2.120	0.370	0.587			2.149	0.370	0.635		
Fe7–S4B	2.309	2.120	0.370	0.600			2.149	0.370	0.649		
Fe7–SG	2.329	2.120	0.370	0.568	2.372	0.372	2.149	0.370	0.615	2.565	-0.435
Fe8–S1	2.363	2.120	0.370	0.519			2.149	0.370	0.561		
Fe8–S3B	2.274	2.120	0.370	0.660			2.149	0.370	0.713		
Fe8–S4B	2.317	2.120	0.370	0.587			2.149	0.370	0.635		
Fe8–SG	2.304	2.120	0.370	0.608	2.373	0.373	2.149	0.370	0.658	2.567	-0.433
					17.741 (P^N)					19.187 (P^N)	

Table S51 The adopted bond valence analyses for irons in P^N [1] from MoFe protein 4WNA which resemble superposition of $P^N/^{2+}$ at 2.0 Å resolution.

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	2.450	2.120	0.370	0.410			2.149	0.370	0.443		
Fe1–S2A	2.267	2.120	0.370	0.672			2.149	0.370	0.727		
Fe1–S4A	2.314	2.120	0.370	0.592			2.149	0.370	0.640		
Fe1–SG	2.359	2.120	0.370	0.524	2.198	0.198	2.149	0.370	0.567	2.377	-0.623
Fe2–S1	2.402	2.120	0.370	0.467			2.149	0.370	0.505		
Fe2–S2A	2.289	2.120	0.370	0.633			2.149	0.370	0.685		
Fe2–S3A	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe2–SG	2.374	2.120	0.370	0.503	2.244	0.244	2.149	0.370	0.544	2.426	-0.574
Fe3–S2A	2.281	2.120	0.370	0.647			2.149	0.370	0.700		
Fe3–S3A	2.250	2.120	0.370	0.704			2.149	0.370	0.761		
Fe3–S4A	2.303	2.120	0.370	0.610			2.149	0.370	0.660		
Fe3–SG	2.293	2.120	0.370	0.627	2.587	0.587	2.149	0.370	0.678	2.798	-0.202
Fe4–S1	2.357	2.120	0.370	0.527			2.149	0.370	0.570		
Fe4–S3A	2.237	2.120	0.370	0.729			2.149	0.370	0.788		
Fe4–S4A	2.300	2.120	0.370	0.615			2.149	0.370	0.665		

Fe4–SG	2.242	2.120	0.370	0.719	2.590	0.590	2.149	0.370	0.778	2.801	-0.199
Fe5–S1(P^N)	3.331	2.120	0.370	0.038			2.149	0.370	0.041		
Fe5–S2B(P^N)	2.236	2.120	0.370	0.731			2.149	0.370	0.790		
Fe5–S4B(P^N)	2.266	2.120	0.370	0.674			2.149	0.370	0.729		
Fe5–SG(P^N)	2.244	2.120	0.370	0.715	2.158 (P^N)	0.158	2.149	0.370	0.774	2.334 (P^N)	-0.666
Fe6–S1(P^N)	3.483	2.120	0.370	0.025			2.149	0.370	0.027		
Fe6–S2B(P^N)	2.297	2.120	0.370	0.620			2.149	0.370	0.670		
Fe6–S3B(P^N)	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe6–SG(P^N)	2.299	2.120	0.370	0.616	1.914 (P^N)	-0.086	2.149	0.370	0.667	2.070 (P^N)	-0.930
Fe7–S2B	2.249	2.120	0.370	0.706			2.149	0.370	0.763		
Fe7–S3B	2.293	2.120	0.370	0.627			2.149	0.370	0.678		
Fe7–S4B	2.275	2.120	0.370	0.658			2.149	0.370	0.711		
Fe7–SG	2.487	2.120	0.370	0.371	2.361	0.361	2.149	0.370	0.401	2.553	-0.447
Fe8–S1	2.382	2.120	0.370	0.493			2.149	0.370	0.533		
Fe8–S3B	2.303	2.120	0.370	0.610			2.149	0.370	0.660		
Fe8–S4B	2.300	2.120	0.370	0.615			2.149	0.370	0.665		
Fe8–SG	2.221	2.120	0.370	0.761	2.478	0.478	2.149	0.370	0.823	2.680	-0.320
					18.530 (P^N)					20.040 (P^N)	

Table S52 The adopted bond valence analyses for irons in P^N [2] from MoFe protein 4WNA which resemble superposition of $P^N/^{2+}$ at 2.0 Å resolution.

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	2.467	2.120	0.370	0.391			2.149	0.370	0.423		
Fe1–S2A	2.279	2.120	0.370	0.651			2.149	0.370	0.704		
Fe1–S4A	2.304	2.120	0.370	0.608			2.149	0.370	0.658		
Fe1–SG	2.397	2.120	0.370	0.473	2.123	0.123	2.149	0.370	0.512	2.296	-0.704
Fe2–S1	2.369	2.120	0.370	0.510			2.149	0.370	0.552		
Fe2–S2A	2.258	2.120	0.370	0.689			2.149	0.370	0.745		
Fe2–S3A	2.268	2.120	0.370	0.670			2.149	0.370	0.725		
Fe2–SG	2.349	2.120	0.370	0.539	2.408	0.408	2.149	0.370	0.582	2.604	-0.396
Fe3–S2A	2.294	2.120	0.370	0.625			2.149	0.370	0.676		
Fe3–S3A	2.228	2.120	0.370	0.747			2.149	0.370	0.808		
Fe3–S4A	2.280	2.120	0.370	0.649			2.149	0.370	0.702		
Fe3–SG	2.241	2.120	0.370	0.721	2.742	0.742	2.149	0.370	0.780	2.965	-0.035
Fe4–S1	2.333	2.120	0.370	0.562			2.149	0.370	0.608		
Fe4–S3A	2.255	2.120	0.370	0.694			2.149	0.370	0.751		
Fe4–S4A	2.307	2.120	0.370	0.603			2.149	0.370	0.652		

Fe4–SG	2.237	2.120	0.370	0.729	2.589	0.589	2.149	0.370	0.788	2.800	-0.200
Fe5–S1(P^N)	3.353	2.120	0.370	0.036			2.149	0.370	0.039		
Fe5–S2B(P^N)	2.226	2.120	0.370	0.751			2.149	0.370	0.812		
Fe5–S4B(P^N)	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe5–SG(P^N)	2.213	2.120	0.370	0.778	2.217 (P^N)	0.217	2.149	0.370	0.841	2.398 (P^N)	-0.602
Fe6–S1(P^N)	3.401	2.120	0.370	0.031			2.149	0.370	0.034		
Fe6–S2B(P^N)	2.310	2.120	0.370	0.598			2.149	0.370	0.647		
Fe6–S3B(P^N)	2.288	2.120	0.370	0.635			2.149	0.370	0.687		
Fe6–SG(P^N)	2.251	2.120	0.370	0.702	1.967 (P^N)	-0.033	2.149	0.370	0.759	2.127 (P^N)	-0.873
Fe7–S2B	2.308	2.120	0.370	0.602			2.149	0.370	0.651		
Fe7–S3B	2.294	2.120	0.370	0.625			2.149	0.370	0.676		
Fe7–S4B	2.260	2.120	0.370	0.685			2.149	0.370	0.741		
Fe7–SG	2.375	2.120	0.370	0.502	2.413	0.413	2.149	0.370	0.543	2.610	-0.390
Fe8–S1	2.374	2.120	0.370	0.503			2.149	0.370	0.544		
Fe8–S3B	2.294	2.120	0.370	0.625			2.149	0.370	0.676		
Fe8–S4B	2.296	2.120	0.370	0.621			2.149	0.370	0.672		
Fe8–SG	2.280	2.120	0.370	0.649	2.399	0.399	2.149	0.370	0.702	2.594	-0.406
					18.857 (P^N)					20.394 (P^N)	

Table S53 The adopted bond valence analyses for irons in P-cluster [1] from MoFe protein 4WZA which was reported as P^N at 1.9 Å resolution.

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	2.495	2.120	0.370	0.363			2.149	0.370	0.393		
Fe1–S2A	2.299	2.120	0.370	0.616			2.149	0.370	0.667		
Fe1–S3A	2.257	2.120	0.370	0.691			2.149	0.370	0.747		
Fe1–SG	2.445	2.120	0.370	0.415	2.085	0.085	2.149	0.370	0.449	2.255	-0.745
Fe2–S1	2.461	2.120	0.370	0.398			2.149	0.370	0.430		
Fe2–S2A	2.307	2.120	0.370	0.603			2.149	0.370	0.652		
Fe2–S4A	2.292	2.120	0.370	0.628			2.149	0.370	0.679		
Fe2–SG	2.425	2.120	0.370	0.439	2.068	0.068	2.149	0.370	0.474	2.236	-0.764
Fe3–S2A	2.309	2.120	0.370	0.600			2.149	0.370	0.649		
Fe3–S3A	2.331	2.120	0.370	0.565			2.149	0.370	0.611		
Fe3–S4A	2.323	2.120	0.370	0.578			2.149	0.370	0.625		
Fe3–SG	2.369	2.120	0.370	0.510	2.253	0.253	2.149	0.370	0.552	2.437	-0.563
Fe4–S1	2.390	2.120	0.370	0.482			2.149	0.370	0.521		
Fe4–S3A	2.270	2.120	0.370	0.667			2.149	0.370	0.721		
Fe4–S4A	2.253	2.120	0.370	0.698			2.149	0.370	0.755		

Fe4–SG	2.414	2.120	0.370	0.452	2.299	0.299	2.149	0.370	0.489	2.486	-0.514
Fe5–S1	2.400	2.120	0.370	0.469			2.149	0.370	0.507		
Fe5–S2B	2.329	2.120	0.370	0.568			2.149	0.370	0.615		
Fe5–S4B	2.250	2.120	0.370	0.704			2.149	0.370	0.761		
Fe5–SG	2.397	2.120	0.370	0.473	2.214	0.214	2.149	0.370	0.512	2.395	-0.605
Fe6–S1	2.488	2.120	0.370	0.370			2.149	0.370	0.400		
Fe6–S2B	2.297	2.120	0.370	0.620			2.149	0.370	0.670		
Fe6–S3B	2.352	2.120	0.370	0.534			2.149	0.370	0.578		
Fe6–SG	2.394	2.120	0.370	0.477	2.001	0.001	2.149	0.370	0.516	2.164	-0.836
Fe7–S2B	2.363	2.120	0.370	0.519			2.149	0.370	0.561		
Fe7–S3B	2.336	2.120	0.370	0.558			2.149	0.370	0.603		
Fe7–S4B	2.361	2.120	0.370	0.521			2.149	0.370	0.564		
Fe7–SG	2.416	2.120	0.370	0.449	2.047	0.047	2.149	0.370	0.486	2.214	-0.786
Fe8–S1	2.412	2.120	0.370	0.454			2.149	0.370	0.491		
Fe8–S3B	2.359	2.120	0.370	0.524			2.149	0.370	0.567		
Fe8–S4B	2.244	2.120	0.370	0.715			2.149	0.370	0.774		
Fe8–SG	2.369	2.120	0.370	0.510	2.204	0.204	2.149	0.370	0.552	2.383	-0.617
					17.171					18.571	

Table S54 The adopted bond valence analyses for irons in P-cluster [2] from MoFe protein 4WZA which was reported as P^N at 1.9 Å resolution.

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	2.464	2.120	0.370	0.395			2.149	0.370	0.427		
Fe1–S2A	2.300	2.120	0.370	0.615			2.149	0.370	0.665		
Fe1–S3A	2.267	2.120	0.370	0.672			2.149	0.370	0.727		
Fe1–SG	2.426	2.120	0.370	0.437	2.119	0.119	2.149	0.370	0.473	2.292	-0.708
Fe2–S1	2.462	2.120	0.370	0.397			2.149	0.370	0.429		
Fe2–S2A	2.322	2.120	0.370	0.579			2.149	0.370	0.627		
Fe2–S4A	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe2–SG	2.413	2.120	0.370	0.453	2.090	0.090	2.149	0.370	0.490	2.261	-0.739
Fe3–S2A	2.307	2.120	0.370	0.603			2.149	0.370	0.652		
Fe3–S3A	2.311	2.120	0.370	0.597			2.149	0.370	0.645		
Fe3–S4A	2.329	2.120	0.370	0.568			2.149	0.370	0.615		
Fe3–SG	2.348	2.120	0.370	0.540	2.308	0.308	2.149	0.370	0.584	2.497	-0.503
Fe4–S1	2.377	2.120	0.370	0.499			2.149	0.370	0.540		
Fe4–S3A	2.267	2.120	0.370	0.672			2.149	0.370	0.727		
Fe4–S4A	2.271	2.120	0.370	0.665			2.149	0.370	0.719		

Fe4–SG	2.428	2.120	0.370	0.435	2.271	0.271	2.149	0.370	0.470	2.456	-0.544
Fe5–S1	2.414	2.120	0.370	0.452			2.149	0.370	0.489		
Fe5–S2B	2.334	2.120	0.370	0.561			2.149	0.370	0.607		
Fe5–S4B	2.272	2.120	0.370	0.663			2.149	0.370	0.717		
Fe5–SG	2.415	2.120	0.370	0.451	2.126	0.126	2.149	0.370	0.487	2.300	-0.700
Fe6–S1	2.488	2.120	0.370	0.370			2.149	0.370	0.400		
Fe6–S2B	2.314	2.120	0.370	0.592			2.149	0.370	0.640		
Fe6–S3B	2.335	2.120	0.370	0.559			2.149	0.370	0.605		
Fe6–SG	2.402	2.120	0.370	0.467	1.988	-0.012	2.149	0.370	0.505	2.150	-0.850
Fe7–S2B	2.359	2.120	0.370	0.524			2.149	0.370	0.567		
Fe7–S3B	2.352	2.120	0.370	0.534			2.149	0.370	0.578		
Fe7–S4B	2.369	2.120	0.370	0.510			2.149	0.370	0.552		
Fe7–SG	2.416	2.120	0.370	0.449	2.018	0.018	2.149	0.370	0.486	2.182	-0.818
Fe8–S1	2.403	2.120	0.370	0.465			2.149	0.370	0.503		
Fe8–S3B	2.325	2.120	0.370	0.575			2.149	0.370	0.621		
Fe8–S4B	2.254	2.120	0.370	0.696			2.149	0.370	0.753		
Fe8–SG	2.426	2.120	0.370	0.437	2.174	0.174	2.149	0.370	0.473	2.351	-0.649
					17.094					18.488	

Table S55 The adopted bond valence analyses for irons in P-cluster [1] from MoFe protein 4WZB which was reported as P^N at 1.9 Å resolution.

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	2.471	2.120	0.370	0.387			2.149	0.370	0.419		
Fe1–S2A	2.275	2.120	0.370	0.658			2.149	0.370	0.711		
Fe1–S3A	2.253	2.120	0.370	0.698			2.149	0.370	0.755		
Fe1–SG	2.465	2.120	0.370	0.394	2.137	0.137	2.149	0.370	0.426	2.311	-0.689
Fe2–S1	2.452	2.120	0.370	0.408			2.149	0.370	0.441		
Fe2–S2A	2.317	2.120	0.370	0.587			2.149	0.370	0.635		
Fe2–S4A	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe2–SG	2.487	2.120	0.370	0.371	2.008	0.008	2.149	0.370	0.401	2.171	-0.829
Fe3–S2A	2.314	2.120	0.370	0.592			2.149	0.370	0.640		
Fe3–S3A	2.289	2.120	0.370	0.633			2.149	0.370	0.685		
Fe3–S4A	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe3–SG	2.511	2.120	0.370	0.348	2.213	0.213	2.149	0.370	0.376	2.394	-0.606
Fe4–S1	2.421	2.120	0.370	0.443			2.149	0.370	0.479		
Fe4–S3A	2.262	2.120	0.370	0.681			2.149	0.370	0.737		
Fe4–S4A	2.248	2.120	0.370	0.708			2.149	0.370	0.765		

Fe4–SG	2.429	2.120	0.370	0.434	2.266	0.266	2.149	0.370	0.469	2.451	-0.549
Fe5–S1	2.398	2.120	0.370	0.472			2.149	0.370	0.510		
Fe5–S2B	2.306	2.120	0.370	0.605			2.149	0.370	0.654		
Fe5–S4B	2.247	2.120	0.370	0.709			2.149	0.370	0.767		
Fe5–SG	2.643	2.120	0.370	0.243	2.029	0.029	2.149	0.370	0.263	2.195	-0.805
Fe6–S1	2.488	2.120	0.370	0.370			2.149	0.370	0.400		
Fe6–S2B	2.296	2.120	0.370	0.621			2.149	0.370	0.672		
Fe6–S3B	2.347	2.120	0.370	0.541			2.149	0.370	0.586		
Fe6–SG	2.488	2.120	0.370	0.370	1.903	-0.097	2.149	0.370	0.400	2.058	-0.942
Fe7–S2B	2.362	2.120	0.370	0.520			2.149	0.370	0.562		
Fe7–S3B	2.328	2.120	0.370	0.570			2.149	0.370	0.616		
Fe7–S4B	2.365	2.120	0.370	0.516			2.149	0.370	0.558		
Fe7–SG	2.498	2.120	0.370	0.360	1.966	-0.034	2.149	0.370	0.389	2.126	-0.874
Fe8–S1	2.413	2.120	0.370	0.453			2.149	0.370	0.490		
Fe8–S3B	2.356	2.120	0.370	0.528			2.149	0.370	0.572		
Fe8–S4B	2.252	2.120	0.370	0.700			2.149	0.370	0.757		
Fe8–SG	2.409	2.120	0.370	0.458	2.139	0.139	2.149	0.370	0.495	2.314	-0.686
					16.660					18.019	

Table S56 The adopted bond valence analyses for irons in P-cluster [2] from MoFe protein 4WZB which was reported as P^N at 2.3 Å resolution.

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	2.463	2.120	0.370	0.396			2.149	0.370	0.428		
Fe1–S2A	2.262	2.120	0.370	0.681			2.149	0.370	0.737		
Fe1–S3A	2.250	2.120	0.370	0.704			2.149	0.370	0.761		
Fe1–SG	2.474	2.120	0.370	0.384	2.165	0.165	2.149	0.370	0.415	2.341	-0.659
Fe2–S1	2.455	2.120	0.370	0.404			2.149	0.370	0.437		
Fe2–S2A	2.342	2.120	0.370	0.549			2.149	0.370	0.594		
Fe2–S4A	2.277	2.120	0.370	0.654			2.149	0.370	0.708		
Fe2–SG	2.510	2.120	0.370	0.349	1.956	-0.044	2.149	0.370	0.377	2.115	-0.885
Fe3–S2A	2.301	2.120	0.370	0.613			2.149	0.370	0.663		
Fe3–S3A	2.325	2.120	0.370	0.575			2.149	0.370	0.621		
Fe3–S4A	2.275	2.120	0.370	0.658			2.149	0.370	0.711		
Fe3–SG	2.430	2.120	0.370	0.433	2.278	0.278	2.149	0.370	0.468	2.464	-0.536
Fe4–S1	2.416	2.120	0.370	0.449			2.149	0.370	0.486		
Fe4–S3A	2.305	2.120	0.370	0.607			2.149	0.370	0.656		
Fe4–S4A	2.247	2.120	0.370	0.709			2.149	0.370	0.767		

Fe4–SG	2.431	2.120	0.370	0.431	2.197	0.197	2.149	0.370	0.467	2.376	-0.624
Fe5–S1	2.431	2.120	0.370	0.431			2.149	0.370	0.467		
Fe5–S2B	2.318	2.120	0.370	0.586			2.149	0.370	0.633		
Fe5–S4B	2.234	2.120	0.370	0.735			2.149	0.370	0.795		
Fe5–SG	2.408	2.120	0.370	0.459	2.211	0.211	2.149	0.370	0.497	2.391	-0.609
Fe6–S1	2.487	2.120	0.370	0.371			2.149	0.370	0.401		
Fe6–S2B	2.288	2.120	0.370	0.635			2.149	0.370	0.687		
Fe6–S3B	2.370	2.120	0.370	0.509			2.149	0.370	0.550		
Fe6–SG	2.531	2.120	0.370	0.329	1.844	-0.156	2.149	0.370	0.356	1.994	-1.006
Fe7–S2B	2.379	2.120	0.370	0.497			2.149	0.370	0.537		
Fe7–S3B	2.303	2.120	0.370	0.610			2.149	0.370	0.660		
Fe7–S4B	2.345	2.120	0.370	0.544			2.149	0.370	0.589		
Fe7–SG	2.430	2.120	0.370	0.433	2.083	0.083	2.149	0.370	0.468	2.253	-0.747
Fe8–S1	2.453	2.120	0.370	0.407			2.149	0.370	0.440		
Fe8–S3B	2.332	2.120	0.370	0.564			2.149	0.370	0.610		
Fe8–S4B	2.212	2.120	0.370	0.780			2.149	0.370	0.843		
Fe8–SG	2.537	2.120	0.370	0.324	2.074	0.074	2.149	0.370	0.350	2.243	-0.757
					16.809					18.179	

Table S57 The adopted bond valence analyses for irons in P-cluster [1] from MoFe protein 5BVG which was reported as P^N at 1.6 Å resolution.

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	2.441	2.120	0.370	0.420			2.149	0.370	0.454		
Fe1–S2A	2.300	2.120	0.370	0.615			2.149	0.370	0.665		
Fe1–S3A	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe1–SG	2.373	2.120	0.370	0.505	2.192	0.192	2.149	0.370	0.546	2.371	-0.629
Fe2–S1	2.415	2.120	0.370	0.451			2.149	0.370	0.487		
Fe2–S2A	2.275	2.120	0.370	0.658			2.149	0.370	0.711		
Fe2–S4A	2.283	2.120	0.370	0.644			2.149	0.370	0.696		
Fe2–SG	2.311	2.120	0.370	0.597	2.349	0.349	2.149	0.370	0.645	2.540	-0.460
Fe3–S2A	2.268	2.120	0.370	0.670			2.149	0.370	0.725		
Fe3–S3A	2.244	2.120	0.370	0.715			2.149	0.370	0.774		
Fe3–S4A	2.318	2.120	0.370	0.586			2.149	0.370	0.633		
Fe3–SG	2.304	2.120	0.370	0.608	2.579	0.579	2.149	0.370	0.658	2.790	-0.210
Fe4–S1	2.394	2.120	0.370	0.477			2.149	0.370	0.516		
Fe4–S3A	2.254	2.120	0.370	0.696			2.149	0.370	0.753		
Fe4–S4A	2.285	2.120	0.370	0.640			2.149	0.370	0.692		

Fe4–SG	2.330	2.120	0.370	0.567	2.380	0.380	2.149	0.370	0.613	2.574	-0.426
Fe5–S1	2.474	2.120	0.370	0.384			2.149	0.370	0.415		
Fe5–S2B	2.232	2.120	0.370	0.739			2.149	0.370	0.799		
Fe5–S4B	2.295	2.120	0.370	0.623			2.149	0.370	0.674		
Fe5–SG	2.341	2.120	0.370	0.550	2.296	0.296	2.149	0.370	0.595	2.484	-0.516
Fe6–S1	2.532	2.120	0.370	0.328			2.149	0.370	0.355		
Fe6–S2B	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe6–S3B	2.322	2.120	0.370	0.579			2.149	0.370	0.627		
Fe6–SG	2.294	2.120	0.370	0.625	2.169	0.169	2.149	0.370	0.676	2.346	-0.654
Fe7–S2B	2.254	2.120	0.370	0.696			2.149	0.370	0.753		
Fe7–S3B	2.318	2.120	0.370	0.586			2.149	0.370	0.633		
Fe7–S4B	2.324	2.120	0.370	0.576			2.149	0.370	0.623		
Fe7–SG	2.387	2.120	0.370	0.486	2.344	0.344	2.149	0.370	0.526	2.535	-0.465
Fe8–S1	2.400	2.120	0.370	0.469			2.149	0.370	0.507		
Fe8–S3B	2.300	2.120	0.370	0.615			2.149	0.370	0.665		
Fe8–S4B	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe8–SG	2.299	2.120	0.370	0.616	2.337	0.337	2.149	0.370	0.667	2.528	-0.472
					16.310					20.167	

Table S58 The adopted bond valence analyses for irons in P-cluster [2] from MoFe protein 5BVG which was reported as P^N at 1.6 Å resolution.

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	2.460	2.120	0.370	0.399			2.149	0.370	0.431		
Fe1–S2A	2.302	2.120	0.370	0.611			2.149	0.370	0.661		
Fe1–S3A	2.295	2.120	0.370	0.623			2.149	0.370	0.674		
Fe1–SG	2.359	2.120	0.370	0.524	2.158	0.158	2.149	0.370	0.567	2.334	-0.666
Fe2–S1	2.420	2.120	0.370	0.444			2.149	0.370	0.481		
Fe2–S2A	2.291	2.120	0.370	0.630			2.149	0.370	0.681		
Fe2–S4A	2.281	2.120	0.370	0.647			2.149	0.370	0.700		
Fe2–SG	2.345	2.120	0.370	0.544	2.266	0.266	2.149	0.370	0.589	2.451	-0.549
Fe3–S2A	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe3–S3A	2.248	2.120	0.370	0.708			2.149	0.370	0.765		
Fe3–S4A	2.322	2.120	0.370	0.579			2.149	0.370	0.627		
Fe3–SG	2.299	2.120	0.370	0.616	2.565	0.565	2.149	0.370	0.667	2.774	-0.226
Fe4–S1	2.377	2.120	0.370	0.499			2.149	0.370	0.540		
Fe4–S3A	2.275	2.120	0.370	0.658			2.149	0.370	0.711		
Fe4–S4A	2.280	2.120	0.370	0.649			2.149	0.370	0.702		

Fe4–SG	2.330	2.120	0.370	0.567	2.373	0.373	2.149	0.370	0.613	2.566	-0.434
Fe5–S1	2.455	2.120	0.370	0.404			2.149	0.370	0.437		
Fe5–S2B	2.239	2.120	0.370	0.725			2.149	0.370	0.784		
Fe5–S4B	2.308	2.120	0.370	0.602			2.149	0.370	0.651		
Fe5–SG	2.332	2.120	0.370	0.564	2.295	0.295	2.149	0.370	0.610	2.482	-0.518
Fe6–S1	2.525	2.120	0.370	0.335			2.149	0.370	0.362		
Fe6–S2B	2.303	2.120	0.370	0.610			2.149	0.370	0.660		
Fe6–S3B	2.309	2.120	0.370	0.600			2.149	0.370	0.649		
Fe6–SG	2.341	2.120	0.370	0.550	2.095	0.095	2.149	0.370	0.595	2.266	-0.734
Fe7–S2B	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe7–S3B	2.330	2.120	0.370	0.567			2.149	0.370	0.613		
Fe7–S4B	2.328	2.120	0.370	0.570			2.149	0.370	0.616		
Fe7–SG	2.358	2.120	0.370	0.526	2.315	0.315	2.149	0.370	0.568	2.504	-0.496
Fe8–S1	2.412	2.120	0.370	0.454			2.149	0.370	0.491		
Fe8–S3B	2.314	2.120	0.370	0.592			2.149	0.370	0.640		
Fe8–S4B	2.312	2.120	0.370	0.595			2.149	0.370	0.644		
Fe8–SG	2.296	2.120	0.370	0.621	2.263	0.263	2.149	0.370	0.672	2.447	-0.553
					16.066					19.823	

Table S59 The adopted bond valence analyses for irons in P-cluster [1] from MoFe protein 5BVH which was reported as P^N at 1.53 Å resolution.

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	2.454	2.120	0.370	0.405			2.149	0.370	0.439		
Fe1–S2A	2.291	2.120	0.370	0.630			2.149	0.370	0.681		
Fe1–S3A	2.277	2.120	0.370	0.654			2.149	0.370	0.708		
Fe1–SG	2.347	2.120	0.370	0.541	2.231	0.231	2.149	0.370	0.586	2.413	-0.587
Fe2–S1	2.438	2.120	0.370	0.423			2.149	0.370	0.458		
Fe2–S2A	2.275	2.120	0.370	0.658			2.149	0.370	0.711		
Fe2–S4A	2.286	2.120	0.370	0.638			2.149	0.370	0.691		
Fe2–SG	2.327	2.120	0.370	0.572	2.291	0.291	2.149	0.370	0.618	2.478	-0.522
Fe3–S2A	2.270	2.120	0.370	0.667			2.149	0.370	0.721		
Fe3–S3A	2.259	2.120	0.370	0.687			2.149	0.370	0.743		
Fe3–S4A	2.330	2.120	0.370	0.567			2.149	0.370	0.613		
Fe3–SG	2.294	2.120	0.370	0.625	2.545	0.545	2.149	0.370	0.676	2.753	-0.247
Fe4–S1	2.416	2.120	0.370	0.449			2.149	0.370	0.486		
Fe4–S3A	2.253	2.120	0.370	0.698			2.149	0.370	0.755		
Fe4–S4A	2.283	2.120	0.370	0.644			2.149	0.370	0.696		

Fe4–SG	2.326	2.120	0.370	0.573	2.364	0.364	2.149	0.370	0.620	2.557	-0.443
Fe5–S1	2.457	2.120	0.370	0.402			2.149	0.370	0.435		
Fe5–S2B	2.265	2.120	0.370	0.676			2.149	0.370	0.731		
Fe5–S4B	2.307	2.120	0.370	0.603			2.149	0.370	0.652		
Fe5–SG	2.349	2.120	0.370	0.539	2.220	0.220	2.149	0.370	0.582	2.401	-0.599
Fe6–S1	2.453	2.120	0.370	0.407			2.149	0.370	0.440		
Fe6–S2B	2.315	2.120	0.370	0.590			2.149	0.370	0.638		
Fe6–S3B	2.321	2.120	0.370	0.581			2.149	0.370	0.628		
Fe6–SG	2.333	2.120	0.370	0.562	2.140	0.140	2.149	0.370	0.608	2.315	-0.685
Fe7–S2B	2.323	2.120	0.370	0.578			2.149	0.370	0.625		
Fe7–S3B	2.311	2.120	0.370	0.597			2.149	0.370	0.645		
Fe7–S4B	2.330	2.120	0.370	0.567			2.149	0.370	0.613		
Fe7–SG	2.349	2.120	0.370	0.539	2.280	0.280	2.149	0.370	0.582	2.466	-0.534
Fe8–S1	2.406	2.120	0.370	0.462			2.149	0.370	0.499		
Fe8–S3B	2.314	2.120	0.370	0.592			2.149	0.370	0.640		
Fe8–S4B	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe8–SG	2.320	2.120	0.370	0.582	2.288	0.288	2.149	0.370	0.630	2.475	-0.525
					18.360					19.857	

Table S60 The adopted bond valence analyses for irons in P-cluster [2] from MoFe protein 5BVH which was reported as P^N at 1.53 Å resolution.

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	2.451	2.120	0.370	0.409			2.149	0.370	0.442		
Fe1–S2A	2.302	2.120	0.370	0.611			2.149	0.370	0.661		
Fe1–S3A	2.277	2.120	0.370	0.654			2.149	0.370	0.708		
Fe1–SG	2.327	2.120	0.370	0.572	2.246	0.246	2.149	0.370	0.618	2.429	-0.571
Fe2–S1	2.420	2.120	0.370	0.444			2.149	0.370	0.481		
Fe2–S2A	2.290	2.120	0.370	0.632			2.149	0.370	0.683		
Fe2–S4A	2.286	2.120	0.370	0.638			2.149	0.370	0.691		
Fe2–SG	2.304	2.120	0.370	0.608	2.323	0.323	2.149	0.370	0.658	2.512	-0.488
Fe3–S2A	2.271	2.120	0.370	0.665			2.149	0.370	0.719		
Fe3–S3A	2.256	2.120	0.370	0.692			2.149	0.370	0.749		
Fe3–S4A	2.323	2.120	0.370	0.578			2.149	0.370	0.625		
Fe3–SG	2.307	2.120	0.370	0.603	2.538	0.538	2.149	0.370	0.652	2.745	-0.255
Fe4–S1	2.392	2.120	0.370	0.479			2.149	0.370	0.519		
Fe4–S3A	2.265	2.120	0.370	0.676			2.149	0.370	0.731		
Fe4–S4A	2.291	2.120	0.370	0.630			2.149	0.370	0.681		

Fe4–SG	2.319	2.120	0.370	0.584	2.369	0.369	2.149	0.370	0.632	2.562	-0.438
Fe5–S1	2.448	2.120	0.370	0.412			2.149	0.370	0.446		
Fe5–S2B	2.247	2.120	0.370	0.709			2.149	0.370	0.767		
Fe5–S4B	2.311	2.120	0.370	0.597			2.149	0.370	0.645		
Fe5–SG	2.369	2.120	0.370	0.510	2.229	0.229	2.149	0.370	0.552	2.410	-0.590
Fe6–S1	2.492	2.120	0.370	0.366			2.149	0.370	0.396		
Fe6–S2B	2.304	2.120	0.370	0.608			2.149	0.370	0.658		
Fe6–S3B	2.306	2.120	0.370	0.605			2.149	0.370	0.654		
Fe6–SG	2.324	2.120	0.370	0.576	2.155	0.155	2.149	0.370	0.623	2.331	-0.669
Fe7–S2B	2.312	2.120	0.370	0.595			2.149	0.370	0.644		
Fe7–S3B	2.310	2.120	0.370	0.598			2.149	0.370	0.647		
Fe7–S4B	2.337	2.120	0.370	0.556			2.149	0.370	0.602		
Fe7–SG	2.358	2.120	0.370	0.526	2.275	0.275	2.149	0.370	0.568	2.461	-0.539
Fe8–S1	2.419	2.120	0.370	0.446			2.149	0.370	0.482		
Fe8–S3B	2.292	2.120	0.370	0.628			2.149	0.370	0.679		
Fe8–S4B	2.302	2.120	0.370	0.611			2.149	0.370	0.661		
Fe8–SG	2.296	2.120	0.370	0.621	2.307	0.307	2.149	0.370	0.672	2.495	-0.505
					18.442					19.946	

Table S61 The adopted bond valence analyses for irons in P-cluster [1] from MoFe protein 5CX1 whose conformation resemble as P^N at 1.75 Å resolution.

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	2.421	2.120	0.370	0.443			2.149	0.370	0.479		
Fe1–S2A	2.249	2.120	0.370	0.706			2.149	0.370	0.763		
Fe1–S3A	2.286	2.120	0.370	0.638			2.149	0.370	0.691		
Fe1–SG	2.334	2.120	0.370	0.561	2.348	0.348	2.149	0.370	0.607	2.540	-0.460
Fe2–S1	2.427	2.120	0.370	0.436			2.149	0.370	0.472		
Fe2–S2A	2.301	2.120	0.370	0.613			2.149	0.370	0.663		
Fe2–S4A	2.259	2.120	0.370	0.687			2.149	0.370	0.743		
Fe2–SG	2.311	2.120	0.370	0.597	2.333	0.333	2.149	0.370	0.645	2.523	-0.477
Fe3–S2A	2.283	2.120	0.370	0.644			2.149	0.370	0.696		
Fe3–S3A	2.265	2.120	0.370	0.676			2.149	0.370	0.731		
Fe3–S4A	2.313	2.120	0.370	0.594			2.149	0.370	0.642		
Fe3–SG	2.301	2.120	0.370	0.613	2.526	0.526	2.149	0.370	0.663	2.732	-0.268
Fe4–S1	2.364	2.120	0.370	0.517			2.149	0.370	0.559		
Fe4–S3A	2.292	2.120	0.370	0.628			2.149	0.370	0.679		
Fe4–S4A	2.289	2.120	0.370	0.633			2.149	0.370	0.685		

Fe4–SG	2.421	2.120	0.370	0.443	2.222	0.222	2.149	0.370	0.479	2.403	-0.597
Fe5–S1	2.478	2.120	0.370	0.380			2.149	0.370	0.411		
Fe5–S2B	2.259	2.120	0.370	0.687			2.149	0.370	0.743		
Fe5–S4B	2.297	2.120	0.370	0.620			2.149	0.370	0.670		
Fe5–SG	2.305	2.120	0.370	0.607	2.293	0.293	2.149	0.370	0.656	2.480	-0.520
Fe6–S1	2.619	2.120	0.370	0.260			2.149	0.370	0.281		
Fe6–S2B	2.268	2.120	0.370	0.670			2.149	0.370	0.725		
Fe6–S3B	2.316	2.120	0.370	0.589			2.149	0.370	0.637		
Fe6–SG	2.328	2.120	0.370	0.570	2.089	0.089	2.149	0.370	0.616	2.259	-0.741
Fe7–S2B	2.286	2.120	0.370	0.638			2.149	0.370	0.691		
Fe7–S3B	2.316	2.120	0.370	0.589			2.149	0.370	0.637		
Fe7–S4B	2.316	2.120	0.370	0.589			2.149	0.370	0.637		
Fe7–SG	2.367	2.120	0.370	0.513	2.329	0.329	2.149	0.370	0.555	2.519	-0.481
Fe8–S1	2.423	2.120	0.370	0.441			2.149	0.370	0.477		
Fe8–S3B	2.270	2.120	0.370	0.667			2.149	0.370	0.721		
Fe8–S4B	2.318	2.120	0.370	0.586			2.149	0.370	0.633		
Fe8–SG	2.307	2.120	0.370	0.603	2.296	0.296	2.149	0.370	0.652	2.484	-0.516
					18.436					19.940	

Table S62 The adopted bond valence analyses for irons in P-cluster [2] from MoFe protein 5CX1 whose conformation resemble as P^N at 1.75 Å resolution.

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	2.441	2.120	0.370	0.420			2.149	0.370	0.454		
Fe1–S2A	2.263	2.120	0.370	0.679			2.149	0.370	0.735		
Fe1–S3A	2.265	2.120	0.370	0.676			2.149	0.370	0.731		
Fe1–SG	2.298	2.120	0.370	0.618	2.393	0.393	2.149	0.370	0.669	2.588	-0.412
Fe2–S1	2.409	2.120	0.370	0.458			2.149	0.370	0.495		
Fe2–S2A	2.291	2.120	0.370	0.630			2.149	0.370	0.681		
Fe2–S4A	2.291	2.120	0.370	0.630			2.149	0.370	0.681		
Fe2–SG	2.310	2.120	0.370	0.598	2.316	0.316	2.149	0.370	0.647	2.505	-0.495
Fe3–S2A	2.296	2.120	0.370	0.621			2.149	0.370	0.672		
Fe3–S3A	2.288	2.120	0.370	0.635			2.149	0.370	0.687		
Fe3–S4A	2.310	2.120	0.370	0.598			2.149	0.370	0.647		
Fe3–SG	2.301	2.120	0.370	0.613	2.468	0.468	2.149	0.370	0.663	2.669	-0.331
Fe4–S1	2.369	2.120	0.370	0.510			2.149	0.370	0.552		
Fe4–S3A	2.295	2.120	0.370	0.623			2.149	0.370	0.674		
Fe4–S4A	2.256	2.120	0.370	0.692			2.149	0.370	0.749		

Fe4–SG	2.402	2.120	0.370	0.467	2.292	0.292	2.149	0.370	0.505	2.479	-0.521
Fe5–S1	2.560	2.120	0.370	0.304			2.149	0.370	0.329		
Fe5–S2B	2.263	2.120	0.370	0.679			2.149	0.370	0.735		
Fe5–S4B	2.313	2.120	0.370	0.594			2.149	0.370	0.642		
Fe5–SG	2.290	2.120	0.370	0.632	2.209	0.209	2.149	0.370	0.683	2.389	-0.611
Fe6–S1	2.626	2.120	0.370	0.255			2.149	0.370	0.275		
Fe6–S2B	2.255	2.120	0.370	0.694			2.149	0.370	0.751		
Fe6–S3B	2.330	2.120	0.370	0.567			2.149	0.370	0.613		
Fe6–SG	2.277	2.120	0.370	0.654	2.170	0.170	2.149	0.370	0.708	2.347	-0.653
Fe7–S2B	2.280	2.120	0.370	0.649			2.149	0.370	0.702		
Fe7–S3B	2.330	2.120	0.370	0.567			2.149	0.370	0.613		
Fe7–S4B	2.281	2.120	0.370	0.647			2.149	0.370	0.700		
Fe7–SG	2.371	2.120	0.370	0.507	2.370	0.370	2.149	0.370	0.549	2.564	-0.436
Fe8–S1	2.407	2.120	0.370	0.460			2.149	0.370	0.498		
Fe8–S3B	2.275	2.120	0.370	0.658			2.149	0.370	0.711		
Fe8–S4B	2.331	2.120	0.370	0.565			2.149	0.370	0.611		
Fe8–SG	2.290	2.120	0.370	0.632	2.315	0.315	2.149	0.370	0.683	2.504	-0.496
					18.535					20.046	

Table S63 The adopted bond valence analyses for irons in P-cluster [3] from MoFe protein 5CX1 whose conformation resemble as P^N at 1.75 Å resolution.

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	2.424	2.120	0.370	0.440			2.149	0.370	0.476		
Fe1–S2A	2.274	2.120	0.370	0.660			2.149	0.370	0.713		
Fe1–S3A	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe1–SG	2.385	2.120	0.370	0.489	2.249	0.249	2.149	0.370	0.528	2.433	-0.567
Fe2–S1	2.414	2.120	0.370	0.452			2.149	0.370	0.489		
Fe2–S2A	2.269	2.120	0.370	0.669			2.149	0.370	0.723		
Fe2–S4A	2.289	2.120	0.370	0.633			2.149	0.370	0.685		
Fe2–SG	2.324	2.120	0.370	0.576	2.330	0.330	2.149	0.370	0.623	2.520	-0.480
Fe3–S2A	2.294	2.120	0.370	0.625			2.149	0.370	0.676		
Fe3–S3A	2.270	2.120	0.370	0.667			2.149	0.370	0.721		
Fe3–S4A	2.304	2.120	0.370	0.608			2.149	0.370	0.658		
Fe3–SG	2.341	2.120	0.370	0.550	2.450	0.450	2.149	0.370	0.595	2.650	-0.350
Fe4–S1	2.386	2.120	0.370	0.487			2.149	0.370	0.527		
Fe4–S3A	2.274	2.120	0.370	0.660			2.149	0.370	0.713		
Fe4–S4A	2.288	2.120	0.370	0.635			2.149	0.370	0.687		

Fe4–SG	2.437	2.120	0.370	0.425	2.206	0.206	2.149	0.370	0.459	2.386	-0.614
Fe5–S1	2.498	2.120	0.370	0.360			2.149	0.370	0.389		
Fe5–S2B	2.225	2.120	0.370	0.753			2.149	0.370	0.814		
Fe5–S4B	2.318	2.120	0.370	0.586			2.149	0.370	0.633		
Fe5–SG	2.327	2.120	0.370	0.572	2.270	0.270	2.149	0.370	0.618	2.455	-0.545
Fe6–S1	2.613	2.120	0.370	0.264			2.149	0.370	0.285		
Fe6–S2B	2.250	2.120	0.370	0.704			2.149	0.370	0.761		
Fe6–S3B	2.321	2.120	0.370	0.581			2.149	0.370	0.628		
Fe6–SG	2.297	2.120	0.370	0.620	2.168	0.168	2.149	0.370	0.670	2.345	-0.655
Fe7–S2B	2.295	2.120	0.370	0.623			2.149	0.370	0.674		
Fe7–S3B	2.320	2.120	0.370	0.582			2.149	0.370	0.630		
Fe7–S4B	2.290	2.120	0.370	0.632			2.149	0.370	0.683		
Fe7–SG	2.390	2.120	0.370	0.482	2.319	0.319	2.149	0.370	0.521	2.508	-0.492
Fe8–S1	2.390	2.120	0.370	0.482			2.149	0.370	0.521		
Fe8–S3B	2.263	2.120	0.370	0.679			2.149	0.370	0.735		
Fe8–S4B	2.329	2.120	0.370	0.568			2.149	0.370	0.615		
Fe8–SG	2.314	2.120	0.370	0.592	2.322	0.322	2.149	0.370	0.640	2.511	-0.489
					18.315					19.808	

Table S64 The adopted bond valence analyses for irons in P-cluster [4] from MoFe protein 5CX1 whose conformation resemble as P^N at 1.75 Å resolution.

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	2.416	2.120	0.370	0.449			2.149	0.370	0.486		
Fe1–S2A	2.294	2.120	0.370	0.625			2.149	0.370	0.676		
Fe1–S3A	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe1–SG	2.393	2.120	0.370	0.478	2.193	0.193	2.149	0.370	0.517	2.371	-0.629
Fe2–S1	2.408	2.120	0.370	0.459			2.149	0.370	0.497		
Fe2–S2A	2.258	2.120	0.370	0.689			2.149	0.370	0.745		
Fe2–S4A	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe2–SG	2.306	2.120	0.370	0.605	2.389	0.389	2.149	0.370	0.654	2.584	-0.416
Fe3–S2A	2.272	2.120	0.370	0.663			2.149	0.370	0.717		
Fe3–S3A	2.260	2.120	0.370	0.685			2.149	0.370	0.741		
Fe3–S4A	2.320	2.120	0.370	0.582			2.149	0.370	0.630		
Fe3–SG	2.294	2.120	0.370	0.625	2.555	0.555	2.149	0.370	0.676	2.764	-0.236
Fe4–S1	2.390	2.120	0.370	0.482			2.149	0.370	0.521		
Fe4–S3A	2.264	2.120	0.370	0.678			2.149	0.370	0.733		
Fe4–S4A	2.275	2.120	0.370	0.658			2.149	0.370	0.711		

Fe4–SG	2.332	2.120	0.370	0.564	2.381	0.381	2.149	0.370	0.610	2.575	-0.425
Fe5–S1	2.463	2.120	0.370	0.396			2.149	0.370	0.428		
Fe5–S2B	2.261	2.120	0.370	0.683			2.149	0.370	0.739		
Fe5–S4B	2.328	2.120	0.370	0.570			2.149	0.370	0.616		
Fe5–SG	2.465	2.120	0.370	0.394	2.042	0.042	2.149	0.370	0.426	2.209	-0.791
Fe6–S1	2.653	2.120	0.370	0.237			2.149	0.370	0.256		
Fe6–S2B	2.258	2.120	0.370	0.689			2.149	0.370	0.745		
Fe6–S3B	2.327	2.120	0.370	0.572			2.149	0.370	0.618		
Fe6–SG	2.309	2.120	0.370	0.600	2.097	0.097	2.149	0.370	0.649	2.268	-0.732
Fe7–S2B	2.295	2.120	0.370	0.623			2.149	0.370	0.674		
Fe7–S3B	2.326	2.120	0.370	0.573			2.149	0.370	0.620		
Fe7–S4B	2.321	2.120	0.370	0.581			2.149	0.370	0.628		
Fe7–SG	2.367	2.120	0.370	0.513	2.290	0.290	2.149	0.370	0.555	2.477	-0.523
Fe8–S1	2.410	2.120	0.370	0.457			2.149	0.370	0.494		
Fe8–S3B	2.315	2.120	0.370	0.590			2.149	0.370	0.638		
Fe8–S4B	2.332	2.120	0.370	0.564			2.149	0.370	0.610		
Fe8–SG	2.305	2.120	0.370	0.607	2.217	0.217	2.149	0.370	0.656	2.398	-0.602
					18.165					19.647	

Table S65 The adopted bond valence analyses for irons in P-cluster [5] from MoFe protein 5CX1 whose conformation resemble as P^N at 1.75 Å resolution.

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	2.425	2.120	0.370	0.439			2.149	0.370	0.474		
Fe1–S2A	2.298	2.120	0.370	0.618			2.149	0.370	0.669		
Fe1–S3A	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe1–SG	2.340	2.120	0.370	0.552	2.270	0.270	2.149	0.370	0.597	2.455	-0.545
Fe2–S1	2.418	2.120	0.370	0.447			2.149	0.370	0.483		
Fe2–S2A	2.295	2.120	0.370	0.623			2.149	0.370	0.674		
Fe2–S4A	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe2–SG	2.304	2.120	0.370	0.608	2.315	0.315	2.149	0.370	0.658	2.504	-0.496
Fe3–S2A	2.266	2.120	0.370	0.674			2.149	0.370	0.729		
Fe3–S3A	2.251	2.120	0.370	0.702			2.149	0.370	0.759		
Fe3–S4A	2.318	2.120	0.370	0.586			2.149	0.370	0.633		
Fe3–SG	2.297	2.120	0.370	0.620	2.581	0.581	2.149	0.370	0.670	2.792	-0.208
Fe4–S1	2.384	2.120	0.370	0.490			2.149	0.370	0.530		
Fe4–S3A	2.270	2.120	0.370	0.667			2.149	0.370	0.721		
Fe4–S4A	2.300	2.120	0.370	0.615			2.149	0.370	0.665		

Fe4–SG	2.415	2.120	0.370	0.451	2.222	0.222	2.149	0.370	0.487	2.403	-0.597
Fe5–S1	2.503	2.120	0.370	0.355			2.149	0.370	0.384		
Fe5–S2B	2.216	2.120	0.370	0.771			2.149	0.370	0.834		
Fe5–S4B	2.328	2.120	0.370	0.570			2.149	0.370	0.616		
Fe5–SG	2.306	2.120	0.370	0.605	2.302	0.302	2.149	0.370	0.654	2.489	-0.511
Fe6–S1	2.584	2.120	0.370	0.285			2.149	0.370	0.309		
Fe6–S2B	2.275	2.120	0.370	0.658			2.149	0.370	0.711		
Fe6–S3B	2.306	2.120	0.370	0.605			2.149	0.370	0.654		
Fe6–SG	2.317	2.120	0.370	0.587	2.135	0.135	2.149	0.370	0.635	2.309	-0.691
Fe7–S2B	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe7–S3B	2.309	2.120	0.370	0.600			2.149	0.370	0.649		
Fe7–S4B	2.291	2.120	0.370	0.630			2.149	0.370	0.681		
Fe7–SG	2.378	2.120	0.370	0.498	2.389	0.389	2.149	0.370	0.539	2.584	-0.416
Fe8–S1	2.416	2.120	0.370	0.449			2.149	0.370	0.486		
Fe8–S3B	2.304	2.120	0.370	0.608			2.149	0.370	0.658		
Fe8–S4B	2.311	2.120	0.370	0.597			2.149	0.370	0.645		
Fe8–SG	2.291	2.120	0.370	0.630	2.284	0.284	2.149	0.370	0.681	2.470	-0.530
					18.498					20.006	

Table S66 The adopted bond valence analyses for irons in P-cluster [6] from MoFe protein 5CX1 whose conformation resemble as P^N at 1.75 Å resolution.

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	2.427	2.120	0.370	0.436			2.149	0.370	0.472		
Fe1–S2A	2.295	2.120	0.370	0.623			2.149	0.370	0.674		
Fe1–S3A	2.239	2.120	0.370	0.725			2.149	0.370	0.784		
Fe1–SG	2.284	2.120	0.370	0.642	2.426	0.426	2.149	0.370	0.694	2.624	-0.376
Fe2–S1	2.391	2.120	0.370	0.481			2.149	0.370	0.520		
Fe2–S2A	2.248	2.120	0.370	0.708			2.149	0.370	0.765		
Fe2–S4A	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe2–SG	2.304	2.120	0.370	0.608	2.433	0.433	2.149	0.370	0.658	2.632	-0.368
Fe3–S2A	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe3–S3A	2.250	2.120	0.370	0.704			2.149	0.370	0.761		
Fe3–S4A	2.319	2.120	0.370	0.584			2.149	0.370	0.632		
Fe3–SG	2.298	2.120	0.370	0.618	2.567	0.567	2.149	0.370	0.669	2.776	-0.224
Fe4–S1	2.362	2.120	0.370	0.520			2.149	0.370	0.562		
Fe4–S3A	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe4–S4A	2.288	2.120	0.370	0.635			2.149	0.370	0.687		

Fe4–SG	2.303	2.120	0.370	0.610	2.405	0.405	2.149	0.370	0.660	2.601	-0.399
Fe5–S1	2.440	2.120	0.370	0.421			2.149	0.370	0.455		
Fe5–S2B	2.230	2.120	0.370	0.743			2.149	0.370	0.803		
Fe5–S4B	2.318	2.120	0.370	0.586			2.149	0.370	0.633		
Fe5–SG	2.427	2.120	0.370	0.436	2.186	0.186	2.149	0.370	0.472	2.364	-0.636
Fe6–S1	2.708	2.120	0.370	0.204			2.149	0.370	0.221		
Fe6–S2B	2.281	2.120	0.370	0.647			2.149	0.370	0.700		
Fe6–S3B	2.303	2.120	0.370	0.610			2.149	0.370	0.660		
Fe6–SG	2.318	2.120	0.370	0.586	2.047	0.047	2.149	0.370	0.633	2.214	-0.786
Fe7–S2B	2.289	2.120	0.370	0.633			2.149	0.370	0.685		
Fe7–S3B	2.327	2.120	0.370	0.572			2.149	0.370	0.618		
Fe7–S4B	2.298	2.120	0.370	0.618			2.149	0.370	0.669		
Fe7–SG	2.363	2.120	0.370	0.519	2.341	0.341	2.149	0.370	0.561	2.532	-0.468
Fe8–S1	2.406	2.120	0.370	0.462			2.149	0.370	0.499		
Fe8–S3B	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe8–S4B	2.309	2.120	0.370	0.600			2.149	0.370	0.649		
Fe8–SG	2.296	2.120	0.370	0.621	2.336	0.336	2.149	0.370	0.672	2.526	-0.474
					18.741					20.269	

Table S67 The adopted bond valence analyses for irons in P-cluster [7] from MoFe protein 5CX1 whose conformation resemble as P^N at 1.75 Å resolution.

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	2.446	2.120	0.370	0.414			2.149	0.370	0.448		
Fe1–S2A	2.268	2.120	0.370	0.670			2.149	0.370	0.725		
Fe1–S3A	2.298	2.120	0.370	0.618			2.149	0.370	0.669		
Fe1–SG	2.339	2.120	0.370	0.553	2.256	0.256	2.149	0.370	0.598	2.440	-0.560
Fe2–S1	2.417	2.120	0.370	0.448			2.149	0.370	0.485		
Fe2–S2A	2.275	2.120	0.370	0.658			2.149	0.370	0.711		
Fe2–S4A	2.249	2.120	0.370	0.706			2.149	0.370	0.763		
Fe2–SG	2.312	2.120	0.370	0.595	2.407	0.407	2.149	0.370	0.644	2.603	-0.397
Fe3–S2A	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe3–S3A	2.260	2.120	0.370	0.685			2.149	0.370	0.741		
Fe3–S4A	2.326	2.120	0.370	0.573			2.149	0.370	0.620		
Fe3–SG	2.324	2.120	0.370	0.576	2.476	0.476	2.149	0.370	0.623	2.678	-0.322
Fe4–S1	2.348	2.120	0.370	0.540			2.149	0.370	0.584		
Fe4–S3A	2.258	2.120	0.370	0.689			2.149	0.370	0.745		
Fe4–S4A	2.275	2.120	0.370	0.658			2.149	0.370	0.711		

Fe4–SG	2.389	2.120	0.370	0.483	2.370	0.370	2.149	0.370	0.523	2.563	-0.437
Fe5–S1	2.510	2.120	0.370	0.349			2.149	0.370	0.377		
Fe5–S2B	2.235	2.120	0.370	0.733			2.149	0.370	0.793		
Fe5–S4B	2.306	2.120	0.370	0.605			2.149	0.370	0.654		
Fe5–SG	2.296	2.120	0.370	0.621	2.308	0.308	2.149	0.370	0.672	2.496	-0.504
Fe6–S1	2.611	2.120	0.370	0.265			2.149	0.370	0.287		
Fe6–S2B	2.251	2.120	0.370	0.702			2.149	0.370	0.759		
Fe6–S3B	2.333	2.120	0.370	0.562			2.149	0.370	0.608		
Fe6–SG	2.295	2.120	0.370	0.623	2.153	0.153	2.149	0.370	0.674	2.328	-0.672
Fe7–S2B	2.266	2.120	0.370	0.674			2.149	0.370	0.729		
Fe7–S3B	2.328	2.120	0.370	0.570			2.149	0.370	0.616		
Fe7–S4B	2.318	2.120	0.370	0.586			2.149	0.370	0.633		
Fe7–SG	2.392	2.120	0.370	0.479	2.309	0.309	2.149	0.370	0.519	2.497	-0.503
Fe8–S1	2.408	2.120	0.370	0.459			2.149	0.370	0.497		
Fe8–S3B	2.290	2.120	0.370	0.632			2.149	0.370	0.683		
Fe8–S4B	2.319	2.120	0.370	0.584			2.149	0.370	0.632		
Fe8–SG	2.303	2.120	0.370	0.610	2.285	0.285	2.149	0.370	0.660	2.471	-0.529
					18.563					20.076	

Table S68 The adopted bond valence analyses for irons in P-cluster [8] from MoFe protein 5CX1 whose conformation resemble as P^N at 1.75 Å resolution.

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	2.447	2.120	0.370	0.413			2.149	0.370	0.447		
Fe1–S2A	2.250	2.120	0.370	0.704			2.149	0.370	0.761		
Fe1–S3A	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe1–SG	2.325	2.120	0.370	0.575	2.344	0.344	2.149	0.370	0.621	2.535	-0.465
Fe2–S1	2.420	2.120	0.370	0.444			2.149	0.370	0.481		
Fe2–S2A	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe2–S4A	2.266	2.120	0.370	0.674			2.149	0.370	0.729		
Fe2–SG	2.299	2.120	0.370	0.616	2.377	0.377	2.149	0.370	0.667	2.571	-0.429
Fe3–S2A	2.281	2.120	0.370	0.647			2.149	0.370	0.700		
Fe3–S3A	2.258	2.120	0.370	0.689			2.149	0.370	0.745		
Fe3–S4A	2.322	2.120	0.370	0.579			2.149	0.370	0.627		
Fe3–SG	2.295	2.120	0.370	0.623	2.538	0.538	2.149	0.370	0.674	2.745	-0.255
Fe4–S1	2.377	2.120	0.370	0.499			2.149	0.370	0.540		
Fe4–S3A	2.308	2.120	0.370	0.602			2.149	0.370	0.651		
Fe4–S4A	2.293	2.120	0.370	0.627			2.149	0.370	0.678		

Fe4–SG	2.327	2.120	0.370	0.572	2.299	0.299	2.149	0.370	0.618	2.486	-0.514
Fe5–S1	2.569	2.120	0.370	0.297			2.149	0.370	0.321		
Fe5–S2B	2.218	2.120	0.370	0.767			2.149	0.370	0.830		
Fe5–S4B	2.292	2.120	0.370	0.628			2.149	0.370	0.679		
Fe5–SG	2.429	2.120	0.370	0.434	2.126	0.126	2.149	0.370	0.469	2.300	-0.700
Fe6–S1	2.597	2.120	0.370	0.275			2.149	0.370	0.298		
Fe6–S2B	2.251	2.120	0.370	0.702			2.149	0.370	0.759		
Fe6–S3B	2.329	2.120	0.370	0.568			2.149	0.370	0.615		
Fe6–SG	2.298	2.120	0.370	0.618	2.164	0.164	2.149	0.370	0.669	2.340	-0.660
Fe7–S2B	2.309	2.120	0.370	0.600			2.149	0.370	0.649		
Fe7–S3B	2.342	2.120	0.370	0.549			2.149	0.370	0.594		
Fe7–S4B	2.303	2.120	0.370	0.610			2.149	0.370	0.660		
Fe7–SG	2.339	2.120	0.370	0.553	2.312	0.312	2.149	0.370	0.598	2.500	-0.500
Fe8–S1	2.375	2.120	0.370	0.502			2.149	0.370	0.543		
Fe8–S3B	2.298	2.120	0.370	0.618			2.149	0.370	0.669		
Fe8–S4B	2.342	2.120	0.370	0.549			2.149	0.370	0.594		
Fe8–SG	2.287	2.120	0.370	0.637	2.306	0.306	2.149	0.370	0.689	2.494	-0.506
					18.466					19.972	

Table S69 The adopted bond valence analyses for irons in P-cluster [1] from MoFe protein 5KOH which is reported as P^N at 1.83 Å resolution.

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	2.491	2.120	0.370	0.367			2.149	0.370	0.397		
Fe1–S2A	2.266	2.120	0.370	0.674			2.149	0.370	0.729		
Fe1–S3A	2.250	2.120	0.370	0.704			2.149	0.370	0.761		
Fe1–SG	2.374	2.120	0.370	0.503	2.248	0.248	2.149	0.370	0.544	2.431	-0.569
Fe2–S1	2.368	2.120	0.370	0.512			2.149	0.370	0.553		
Fe2–S2A	2.307	2.120	0.370	0.603			2.149	0.370	0.652		
Fe2–S4A	2.300	2.120	0.370	0.615			2.149	0.370	0.665		
Fe2–SG	2.319	2.120	0.370	0.584	2.314	0.314	2.149	0.370	0.632	2.502	-0.498
Fe3–S2A	2.305	2.120	0.370	0.607			2.149	0.370	0.656		
Fe3–S3A	2.262	2.120	0.370	0.681			2.149	0.370	0.737		
Fe3–S4A	2.320	2.120	0.370	0.582			2.149	0.370	0.630		
Fe3–SG	2.251	2.120	0.370	0.702	2.572	0.572	2.149	0.370	0.759	2.782	-0.218
Fe4–S1	2.341	2.120	0.370	0.550			2.149	0.370	0.595		
Fe4–S3A	2.297	2.120	0.370	0.620			2.149	0.370	0.670		
Fe4–S4A	2.282	2.120	0.370	0.645			2.149	0.370	0.698		

Fe4–SG	2.310	2.120	0.370	0.598	2.414	0.414	2.149	0.370	0.647	2.611	-0.389
Fe5–S1	2.491	2.120	0.370	0.367			2.149	0.370	0.397		
Fe5–S2B	2.280	2.120	0.370	0.649			2.149	0.370	0.702		
Fe5–S4B	2.301	2.120	0.370	0.613			2.149	0.370	0.663		
Fe5–SG	2.319	2.120	0.370	0.584	2.213	0.213	2.149	0.370	0.632	2.393	-0.607
Fe6–S1	2.515	2.120	0.370	0.344			2.149	0.370	0.372		
Fe6–S2B	2.314	2.120	0.370	0.592			2.149	0.370	0.640		
Fe6–S3B	2.307	2.120	0.370	0.603			2.149	0.370	0.652		
Fe6–SG	2.317	2.120	0.370	0.587	2.126	0.126	2.149	0.370	0.635	2.300	-0.700
Fe7–S2B	2.294	2.120	0.370	0.625			2.149	0.370	0.676		
Fe7–S3B	2.308	2.120	0.370	0.602			2.149	0.370	0.651		
Fe7–S4B	2.343	2.120	0.370	0.547			2.149	0.370	0.592		
Fe7–SG	2.333	2.120	0.370	0.562	2.336	0.336	2.149	0.370	0.608	2.527	-0.473
Fe8–S1	2.503	2.120	0.370	0.355			2.149	0.370	0.384		
Fe8–S3B	2.290	2.120	0.370	0.632			2.149	0.370	0.683		
Fe8–S4B	2.298	2.120	0.370	0.618			2.149	0.370	0.669		
Fe8–SG	2.252	2.120	0.370	0.700	2.305	0.305	2.149	0.370	0.757	2.493	-0.507
					18.528					20.038	

Table S70 The adopted bond valence analyses for irons in P-cluster [2] from MoFe protein 5KOH which is reported as P^N at 1.83 Å resolution.

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	2.500	2.120	0.370	0.358			2.149	0.370	0.387		
Fe1–S2A	2.306	2.120	0.370	0.605			2.149	0.370	0.654		
Fe1–S3A	2.240	2.120	0.370	0.723			2.149	0.370	0.782		
Fe1–SG	2.356	2.120	0.370	0.528	2.214	0.214	2.149	0.370	0.572	2.395	-0.605
Fe2–S1	2.395	2.120	0.370	0.476			2.149	0.370	0.514		
Fe2–S2A	2.286	2.120	0.370	0.638			2.149	0.370	0.691		
Fe2–S4A	2.288	2.120	0.370	0.635			2.149	0.370	0.687		
Fe2–SG	2.321	2.120	0.370	0.581	2.330	0.330	2.149	0.370	0.628	2.520	-0.480
Fe3–S2A	2.275	2.120	0.370	0.658			2.149	0.370	0.711		
Fe3–S3A	2.280	2.120	0.370	0.649			2.149	0.370	0.702		
Fe3–S4A	2.306	2.120	0.370	0.605			2.149	0.370	0.654		
Fe3–SG	2.306	2.120	0.370	0.605	2.516	0.516	2.149	0.370	0.654	2.722	-0.278
Fe4–S1	2.368	2.120	0.370	0.512			2.149	0.370	0.553		
Fe4–S3A	2.274	2.120	0.370	0.660			2.149	0.370	0.713		
Fe4–S4A	2.265	2.120	0.370	0.676			2.149	0.370	0.731		

Fe4–SG	2.326	2.120	0.370	0.573	2.420	0.420	2.149	0.370	0.620	2.617	-0.383
Fe5–S1	2.455	2.120	0.370	0.404			2.149	0.370	0.437		
Fe5–S2B	2.272	2.120	0.370	0.663			2.149	0.370	0.717		
Fe5–S4B	2.313	2.120	0.370	0.594			2.149	0.370	0.642		
Fe5–SG	2.366	2.120	0.370	0.514	2.175	0.175	2.149	0.370	0.556	2.353	-0.647
Fe6–S1	2.493	2.120	0.370	0.365			2.149	0.370	0.395		
Fe6–S2B	2.297	2.120	0.370	0.620			2.149	0.370	0.670		
Fe6–S3B	2.317	2.120	0.370	0.587			2.149	0.370	0.635		
Fe6–SG	2.369	2.120	0.370	0.510	2.082	0.082	2.149	0.370	0.552	2.252	-0.748
Fe7–S2B	2.289	2.120	0.370	0.633			2.149	0.370	0.685		
Fe7–S3B	2.295	2.120	0.370	0.623			2.149	0.370	0.674		
Fe7–S4B	2.335	2.120	0.370	0.559			2.149	0.370	0.605		
Fe7–SG	2.335	2.120	0.370	0.559	2.375	0.375	2.149	0.370	0.605	2.569	-0.431
Fe8–S1	2.493	2.120	0.370	0.365			2.149	0.370	0.395		
Fe8–S3B	2.310	2.120	0.370	0.598			2.149	0.370	0.647		
Fe8–S4B	2.312	2.120	0.370	0.595			2.149	0.370	0.644		
Fe8–SG	2.235	2.120	0.370	0.733	2.291	0.291	2.149	0.370	0.793	2.478	-0.522
					18.405					19.905	

Table S71 The adopted bond valence analyses for irons in P-cluster [1] from MoFe protein 5VPW which is reported as P^N at 1.85 Å resolution.

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	2.389	2.120	0.370	0.483			2.149	0.370	0.523		
Fe1–S2A	2.316	2.120	0.370	0.589			2.149	0.370	0.637		
Fe1–S3A	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe1–SG	2.321	2.120	0.370	0.581	2.305	0.305	2.149	0.370	0.628	2.493	-0.507
Fe2–S1	2.415	2.120	0.370	0.451			2.149	0.370	0.487		
Fe2–S2A	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe2–S4A	2.281	2.120	0.370	0.647			2.149	0.370	0.700		
Fe2–SG	2.314	2.120	0.370	0.592	2.351	0.351	2.149	0.370	0.640	2.543	-0.457
Fe3–S2A	2.293	2.120	0.370	0.627			2.149	0.370	0.678		
Fe3–S3A	2.331	2.120	0.370	0.565			2.149	0.370	0.611		
Fe3–S4A	2.288	2.120	0.370	0.635			2.149	0.370	0.687		
Fe3–SG	2.287	2.120	0.370	0.637	2.464	0.464	2.149	0.370	0.689	2.665	-0.335
Fe4–S1	2.402	2.120	0.370	0.467			2.149	0.370	0.505		
Fe4–S3A	2.242	2.120	0.370	0.719			2.149	0.370	0.778		
Fe4–S4A	2.236	2.120	0.370	0.731			2.149	0.370	0.790		

Fe4–SG	2.382	2.120	0.370	0.493	2.409	0.409	2.149	0.370	0.533	2.606	-0.394
Fe5–S1	2.545	2.120	0.370	0.317			2.149	0.370	0.343		
Fe5–S2B	2.400	2.120	0.370	0.469			2.149	0.370	0.507		
Fe5–S4B	2.245	2.120	0.370	0.713			2.149	0.370	0.771		
Fe5–SG	2.333	2.120	0.370	0.562	2.062	0.062	2.149	0.370	0.608	2.230	-0.770
Fe6–S1	2.565	2.120	0.370	0.300			2.149	0.370	0.325		
Fe6–S2B	2.441	2.120	0.370	0.420			2.149	0.370	0.454		
Fe6–S3B	2.317	2.120	0.370	0.587			2.149	0.370	0.635		
Fe6–SG	2.324	2.120	0.370	0.576	1.884	-0.116	2.149	0.370	0.623	2.037	-0.963
Fe7–S2B	2.313	2.120	0.370	0.594			2.149	0.370	0.642		
Fe7–S3B	2.323	2.120	0.370	0.578			2.149	0.370	0.625		
Fe7–S4B	2.336	2.120	0.370	0.558			2.149	0.370	0.603		
Fe7–SG	2.298	2.120	0.370	0.618	2.347	0.347	2.149	0.370	0.669	2.539	-0.461
Fe8–S1	2.369	2.120	0.370	0.510			2.149	0.370	0.552		
Fe8–S3B	2.317	2.120	0.370	0.587			2.149	0.370	0.635		
Fe8–S4B	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe8–SG	2.391	2.120	0.370	0.481	2.215	0.215	2.149	0.370	0.520	2.395	-0.605
					18.037					19.508	

Table S72 The adopted bond valence analyses for irons in P-cluster [2] from MoFe protein 5VPW which is reported as P^N at 1.85 Å resolution.

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	2.416	2.120	0.370	0.449			2.149	0.370	0.486		
Fe1–S2A	2.298	2.120	0.370	0.618			2.149	0.370	0.669		
Fe1–S3A	2.299	2.120	0.370	0.616			2.149	0.370	0.667		
Fe1–SG	2.342	2.120	0.370	0.549	2.233	0.233	2.149	0.370	0.594	2.415	-0.585
Fe2–S1	2.470	2.120	0.370	0.388			2.149	0.370	0.420		
Fe2–S2A	2.289	2.120	0.370	0.633			2.149	0.370	0.685		
Fe2–S4A	2.300	2.120	0.370	0.615			2.149	0.370	0.665		
Fe2–SG	2.334	2.120	0.370	0.561	2.197	0.197	2.149	0.370	0.607	2.376	-0.624
Fe3–S2A	2.293	2.120	0.370	0.627			2.149	0.370	0.678		
Fe3–S3A	2.318	2.120	0.370	0.586			2.149	0.370	0.633		
Fe3–S4A	2.291	2.120	0.370	0.630			2.149	0.370	0.681		
Fe3–SG	2.321	2.120	0.370	0.581	2.423	0.423	2.149	0.370	0.628	2.620	-0.380
Fe4–S1	2.371	2.120	0.370	0.507			2.149	0.370	0.549		
Fe4–S3A	2.324	2.120	0.370	0.576			2.149	0.370	0.623		
Fe4–S4A	2.259	2.120	0.370	0.687			2.149	0.370	0.743		

Fe4–SG	2.307	2.120	0.370	0.603	2.374	0.374	2.149	0.370	0.652	2.567	-0.433
Fe5–S1	2.542	2.120	0.370	0.320			2.149	0.370	0.346		
Fe5–S2B	2.349	2.120	0.370	0.539			2.149	0.370	0.582		
Fe5–S4B	2.283	2.120	0.370	0.644			2.149	0.370	0.696		
Fe5–SG	2.297	2.120	0.370	0.620	2.122	0.122	2.149	0.370	0.670	2.295	-0.705
Fe6–S1	2.524	2.120	0.370	0.336			2.149	0.370	0.363		
Fe6–S2B	2.428	2.120	0.370	0.435			2.149	0.370	0.470		
Fe6–S3B	2.314	2.120	0.370	0.592			2.149	0.370	0.640		
Fe6–SG	2.337	2.120	0.370	0.556	1.919	-0.081	2.149	0.370	0.602	2.075	-0.925
Fe7–S2B	2.356	2.120	0.370	0.528			2.149	0.370	0.572		
Fe7–S3B	2.331	2.120	0.370	0.565			2.149	0.370	0.611		
Fe7–S4B	2.320	2.120	0.370	0.582			2.149	0.370	0.630		
Fe7–SG	2.333	2.120	0.370	0.562	2.239	0.239	2.149	0.370	0.608	2.421	-0.579
Fe8–S1	2.367	2.120	0.370	0.513			2.149	0.370	0.555		
Fe8–S3B	2.300	2.120	0.370	0.615			2.149	0.370	0.665		
Fe8–S4B	2.313	2.120	0.370	0.594			2.149	0.370	0.642		
Fe8–SG	2.367	2.120	0.370	0.513	2.234	0.234	2.149	0.370	0.555	2.416	-0.584
					17.740					19.186	

Table S73 The adopted bond valence analyses for irons in P-cluster [1] from MoFe protein 5VQ3 which is reported as P^N at 1.72 Å resolution.

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	2.419	2.120	0.370	0.446			2.149	0.370	0.482		
Fe1–S2A	2.332	2.120	0.370	0.564			2.149	0.370	0.610		
Fe1–S3A	2.293	2.120	0.370	0.627			2.149	0.370	0.678		
Fe1–SG	2.303	2.120	0.370	0.610	2.246	0.246	2.149	0.370	0.660	2.429	-0.571
Fe2–S1	2.470	2.120	0.370	0.388			2.149	0.370	0.420		
Fe2–S2A	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe2–S4A	2.299	2.120	0.370	0.616			2.149	0.370	0.667		
Fe2–SG	2.350	2.120	0.370	0.537	2.179	0.179	2.149	0.370	0.581	2.356	-0.644
Fe3–S2A	2.325	2.120	0.370	0.575			2.149	0.370	0.621		
Fe3–S3A	2.318	2.120	0.370	0.586			2.149	0.370	0.633		
Fe3–S4A	2.288	2.120	0.370	0.635			2.149	0.370	0.687		
Fe3–SG	2.288	2.120	0.370	0.635	2.430	0.430	2.149	0.370	0.687	2.628	-0.372
Fe4–S1	2.401	2.120	0.370	0.468			2.149	0.370	0.506		
Fe4–S3A	2.257	2.120	0.370	0.691			2.149	0.370	0.747		
Fe4–S4A	2.254	2.120	0.370	0.696			2.149	0.370	0.753		

Fe4–SG	2.331	2.120	0.370	0.565	2.420	0.420	2.149	0.370	0.611	2.617	-0.383
Fe5–S1	2.485	2.120	0.370	0.373			2.149	0.370	0.403		
Fe5–S2B	2.348	2.120	0.370	0.540			2.149	0.370	0.584		
Fe5–S4B	2.253	2.120	0.370	0.698			2.149	0.370	0.755		
Fe5–SG	2.340	2.120	0.370	0.552	2.163	0.163	2.149	0.370	0.597	2.339	-0.661
Fe6–S1	2.484	2.120	0.370	0.374			2.149	0.370	0.404		
Fe6–S2B	2.408	2.120	0.370	0.459			2.149	0.370	0.497		
Fe6–S3B	2.340	2.120	0.370	0.552			2.149	0.370	0.597		
Fe6–SG	2.308	2.120	0.370	0.602	1.986	-0.014	2.149	0.370	0.651	2.148	-0.852
Fe7–S2B	2.319	2.120	0.370	0.584			2.149	0.370	0.632		
Fe7–S3B	2.342	2.120	0.370	0.549			2.149	0.370	0.594		
Fe7–S4B	2.336	2.120	0.370	0.558			2.149	0.370	0.603		
Fe7–SG	2.253	2.120	0.370	0.698	2.389	0.389	2.149	0.370	0.755	2.583	-0.417
Fe8–S1	2.398	2.120	0.370	0.472			2.149	0.370	0.510		
Fe8–S3B	2.297	2.120	0.370	0.620			2.149	0.370	0.670		
Fe8–S4B	2.313	2.120	0.370	0.594			2.149	0.370	0.642		
Fe8–SG	2.346	2.120	0.370	0.543	2.228	0.228	2.149	0.370	0.587	2.410	-0.590
					18.041					19.511	

Table S74 The adopted bond valence analyses for irons in P-cluster [2] from MoFe protein 5VQ3 which is reported as P^N at 1.72 Å resolution.

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	2.415	2.120	0.370	0.451			2.149	0.370	0.487		
Fe1–S2A	2.330	2.120	0.370	0.567			2.149	0.370	0.613		
Fe1–S3A	2.310	2.120	0.370	0.598			2.149	0.370	0.647		
Fe1–SG	2.336	2.120	0.370	0.558	2.174	0.174	2.149	0.370	0.603	2.351	-0.649
Fe2–S1	2.479	2.120	0.370	0.379			2.149	0.370	0.410		
Fe2–S2A	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe2–S4A	2.316	2.120	0.370	0.589			2.149	0.370	0.637		
Fe2–SG	2.322	2.120	0.370	0.579	2.199	0.199	2.149	0.370	0.627	2.379	-0.621
Fe3–S2A	2.313	2.120	0.370	0.594			2.149	0.370	0.642		
Fe3–S3A	2.317	2.120	0.370	0.587			2.149	0.370	0.635		
Fe3–S4A	2.268	2.120	0.370	0.670			2.149	0.370	0.725		
Fe3–SG	2.305	2.120	0.370	0.607	2.458	0.458	2.149	0.370	0.656	2.658	-0.342
Fe4–S1	2.381	2.120	0.370	0.494			2.149	0.370	0.534		
Fe4–S3A	2.299	2.120	0.370	0.616			2.149	0.370	0.667		
Fe4–S4A	2.294	2.120	0.370	0.625			2.149	0.370	0.676		

Fe4–SG	2.332	2.120	0.370	0.564	2.299	0.299	2.149	0.370	0.610	2.486	-0.514
Fe5–S1	2.483	2.120	0.370	0.375			2.149	0.370	0.405		
Fe5–S2B	2.312	2.120	0.370	0.595			2.149	0.370	0.644		
Fe5–S4B	2.288	2.120	0.370	0.635			2.149	0.370	0.687		
Fe5–SG	2.348	2.120	0.370	0.540	2.145	0.145	2.149	0.370	0.584	2.320	-0.680
Fe6–S1	2.477	2.120	0.370	0.381			2.149	0.370	0.412		
Fe6–S2B	2.411	2.120	0.370	0.455			2.149	0.370	0.493		
Fe6–S3B	2.297	2.120	0.370	0.620			2.149	0.370	0.670		
Fe6–SG	2.278	2.120	0.370	0.652	2.109	0.109	2.149	0.370	0.706	2.281	-0.719
Fe7–S2B	2.326	2.120	0.370	0.573			2.149	0.370	0.620		
Fe7–S3B	2.306	2.120	0.370	0.605			2.149	0.370	0.654		
Fe7–S4B	2.298	2.120	0.370	0.618			2.149	0.370	0.669		
Fe7–SG	2.323	2.120	0.370	0.578	2.374	0.374	2.149	0.370	0.625	2.567	-0.433
Fe8–S1	2.387	2.120	0.370	0.486			2.149	0.370	0.526		
Fe8–S3B	2.271	2.120	0.370	0.665			2.149	0.370	0.719		
Fe8–S4B	2.315	2.120	0.370	0.590			2.149	0.370	0.638		
Fe8–SG	2.287	2.120	0.370	0.637	2.378	0.378	2.149	0.370	0.689	2.572	-0.428
					18.135					19.614	

Table S75 The adopted bond valence analyses for irons in P-cluster [1] from MoFe protein 5VQ4 whose conformation resemble P^N at 2.3 Å resolution.

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	2.449	2.120	0.370	0.411			2.149	0.370	0.444		
Fe1–S2A	2.329	2.120	0.370	0.568			2.149	0.370	0.615		
Fe1–S3A	2.308	2.120	0.370	0.602			2.149	0.370	0.651		
Fe1–SG	2.287	2.120	0.370	0.637	2.218	0.218	2.149	0.370	0.689	2.399	-0.601
Fe2–S1	2.506	2.120	0.370	0.352			2.149	0.370	0.381		
Fe2–S2A	2.288	2.120	0.370	0.635			2.149	0.370	0.687		
Fe2–S4A	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe2–SG	2.272	2.120	0.370	0.663	2.287	0.287	2.149	0.370	0.717	2.474	-0.526
Fe3–S2A	2.281	2.120	0.370	0.647			2.149	0.370	0.700		
Fe3–S3A	2.311	2.120	0.370	0.597			2.149	0.370	0.645		
Fe3–S4A	2.272	2.120	0.370	0.663			2.149	0.370	0.717		
Fe3–SG	2.232	2.120	0.370	0.739	2.646	0.646	2.149	0.370	0.799	2.862	-0.138
Fe4–S1	2.374	2.120	0.370	0.503			2.149	0.370	0.544		
Fe4–S3A	2.314	2.120	0.370	0.592			2.149	0.370	0.640		
Fe4–S4A	2.315	2.120	0.370	0.590			2.149	0.370	0.638		

Fe4–SG	2.199	2.120	0.370	0.808	2.493	0.493	2.149	0.370	0.874	2.697	-0.303
Fe5–S1	2.738	2.120	0.370	0.188			2.149	0.370	0.204		
Fe5–S2B	2.355	2.120	0.370	0.530			2.149	0.370	0.573		
Fe5–S4B	2.238	2.120	0.370	0.727			2.149	0.370	0.786		
Fe5–SG	2.312	2.120	0.370	0.595	2.040	0.040	2.149	0.370	0.644	2.206	-0.794
Fe6–S1	2.978	2.120	0.370	0.098			2.149	0.370	0.106		
Fe6–S2B	2.419	2.120	0.370	0.446			2.149	0.370	0.482		
Fe6–S3B	2.348	2.120	0.370	0.540			2.149	0.370	0.584		
Fe6–SG	2.278	2.120	0.370	0.652	1.737	-0.263	2.149	0.370	0.706	1.878	-1.122
Fe7–S2B	2.314	2.120	0.370	0.592			2.149	0.370	0.640		
Fe7–S3B	2.297	2.120	0.370	0.620			2.149	0.370	0.670		
Fe7–S4B	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe7–SG	2.306	2.120	0.370	0.605	2.457	0.457	2.149	0.370	0.654	2.657	-0.343
Fe8–S1	2.353	2.120	0.370	0.533			2.149	0.370	0.576		
Fe8–S3B	2.281	2.120	0.370	0.647			2.149	0.370	0.700		
Fe8–S4B	2.282	2.120	0.370	0.645			2.149	0.370	0.698		
Fe8–SG	2.198	2.120	0.370	0.810	2.635	0.635	2.149	0.370	0.876	2.850	-0.150
					18.513					20.023	

Table S76 The adopted bond valence analyses for irons in P-cluster [2] from MoFe protein 5VQ4 whose conformation resemble P^N at 2.3 Å resolution.

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	2.422	2.120	0.370	0.442			2.149	0.370	0.478		
Fe1–S2A	2.335	2.120	0.370	0.559			2.149	0.370	0.605		
Fe1–S3A	2.335	2.120	0.370	0.559			2.149	0.370	0.605		
Fe1–SG	2.403	2.120	0.370	0.465	2.026	0.026	2.149	0.370	0.503	2.191	-0.809
Fe2–S1	2.473	2.120	0.370	0.385			2.149	0.370	0.417		
Fe2–S2A	2.296	2.120	0.370	0.621			2.149	0.370	0.672		
Fe2–S4A	2.293	2.120	0.370	0.627			2.149	0.370	0.678		
Fe2–SG	2.307	2.120	0.370	0.603	2.236	0.236	2.149	0.370	0.652	2.419	-0.581
Fe3–S2A	2.338	2.120	0.370	0.555			2.149	0.370	0.600		
Fe3–S3A	2.296	2.120	0.370	0.621			2.149	0.370	0.672		
Fe3–S4A	2.243	2.120	0.370	0.717			2.149	0.370	0.776		
Fe3–SG	2.277	2.120	0.370	0.654	2.548	0.548	2.149	0.370	0.708	2.755	-0.245
Fe4–S1	2.400	2.120	0.370	0.469			2.149	0.370	0.507		
Fe4–S3A	2.325	2.120	0.370	0.575			2.149	0.370	0.621		
Fe4–S4A	2.280	2.120	0.370	0.649			2.149	0.370	0.702		

Fe4–SG	2.207	2.120	0.370	0.790	2.483	0.483	2.149	0.370	0.855	2.686	-0.314
Fe5–S1	2.724	2.120	0.370	0.195			2.149	0.370	0.211		
Fe5–S2B	2.375	2.120	0.370	0.502			2.149	0.370	0.543		
Fe5–S4B	2.218	2.120	0.370	0.767			2.149	0.370	0.830		
Fe5–SG	2.325	2.120	0.370	0.575	2.039	0.039	2.149	0.370	0.621	2.206	-0.794
Fe6–S1	2.936	2.120	0.370	0.110			2.149	0.370	0.119		
Fe6–S2B	2.439	2.120	0.370	0.422			2.149	0.370	0.457		
Fe6–S3B	2.312	2.120	0.370	0.595			2.149	0.370	0.644		
Fe6–SG	2.304	2.120	0.370	0.608	1.736	-0.264	2.149	0.370	0.658	1.877	-1.123
Fe7–S2B	2.311	2.120	0.370	0.597			2.149	0.370	0.645		
Fe7–S3B	2.336	2.120	0.370	0.558			2.149	0.370	0.603		
Fe7–S4B	2.290	2.120	0.370	0.632			2.149	0.370	0.683		
Fe7–SG	2.515	2.120	0.370	0.344	2.130	0.130	2.149	0.370	0.372	2.304	-0.696
Fe8–S1	2.360	2.120	0.370	0.523			2.149	0.370	0.565		
Fe8–S3B	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe8–S4B	2.323	2.120	0.370	0.578			2.149	0.370	0.625		
Fe8–SG	2.359	2.120	0.370	0.524	2.286	0.286	2.149	0.370	0.567	2.472	-0.528
					17.484					18.910	

Table S77 The adopted bond valence analyses for irons in P-cluster [1] from MoFe protein 6O7L whose conformations resemble P^N at 2.26 Å resolution.

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	2.453	2.120	0.370	0.407			2.149	0.370	0.440		
Fe1–S2A	2.229	2.120	0.370	0.745			2.149	0.370	0.806		
Fe1–S3A	2.222	2.120	0.370	0.759			2.149	0.370	0.821		
Fe1–SG	2.503	2.120	0.370	0.355	2.266	0.266	2.149	0.370	0.384	2.450	-0.550
Fe2–S1	2.395	2.120	0.370	0.476			2.149	0.370	0.514		
Fe2–S2A	2.244	2.120	0.370	0.715			2.149	0.370	0.774		
Fe2–S4A	2.223	2.120	0.370	0.757			2.149	0.370	0.819		
Fe2–SG	2.421	2.120	0.370	0.443	2.391	0.391	2.149	0.370	0.479	2.586	-0.414
Fe3–S2A	2.225	2.120	0.370	0.753			2.149	0.370	0.814		
Fe3–S3A	2.217	2.120	0.370	0.769			2.149	0.370	0.832		
Fe3–S4A	2.290	2.120	0.370	0.632			2.149	0.370	0.683		
Fe3–SG	2.296	2.120	0.370	0.621	2.775	0.775	2.149	0.370	0.672	3.002	0.002
Fe4–S1	2.297	2.120	0.370	0.620			2.149	0.370	0.670		
Fe4–S3A	2.229	2.120	0.370	0.745			2.149	0.370	0.806		
Fe4–S4A	2.246	2.120	0.370	0.711			2.149	0.370	0.769		

Fe4–SG	2.414	2.120	0.370	0.452	2.528	0.528	2.149	0.370	0.489	2.734	-0.266
Fe5–S1	2.480	2.120	0.370	0.378			2.149	0.370	0.409		
Fe5–S2B	2.007	2.120	0.370	1.357			2.149	0.370	1.468		
Fe5–S4B	2.238	2.120	0.370	0.727			2.149	0.370	0.786		
Fe5–SG	2.366	2.120	0.370	0.514	2.976	0.976	2.149	0.370	0.556	3.219	0.219
Fe6–S1	2.849	2.120	0.370	0.139			2.149	0.370	0.151		
Fe6–S2B	2.245	2.120	0.370	0.713			2.149	0.370	0.771		
Fe6–S3B	2.292	2.120	0.370	0.628			2.149	0.370	0.679		
Fe6–SG	2.253	2.120	0.370	0.698	2.179	0.179	2.149	0.370	0.755	2.357	-0.643
Fe7–S2B	2.572	2.120	0.370	0.295			2.149	0.370	0.319		
Fe7–S3B	2.533	2.120	0.370	0.328			2.149	0.370	0.354		
Fe7–S4B	2.494	2.120	0.370	0.364			2.149	0.370	0.394		
Fe7–SG	2.256	2.120	0.370	0.692	1.679	-0.321	2.149	0.370	0.749	1.815	-1.185
Fe8–S1	2.251	2.120	0.370	0.702			2.149	0.370	0.759		
Fe8–S3B	2.132	2.120	0.370	0.968			2.149	0.370	1.047		
Fe8–S4B	2.321	2.120	0.370	0.581			2.149	0.370	0.628		
Fe8–SG	2.486	2.120	0.370	0.372	2.623	0.623	2.149	0.370	0.402	2.836	-0.164
					19.417					21.000	

Table S78 The adopted bond valence analyses for irons in P-cluster [2] from MoFe protein 6O7L whose conformations resemble P^N at 2.26 Å resolution.

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	2.484	2.120	0.370	0.374			2.149	0.370	0.404		
Fe1–S2A	2.268	2.120	0.370	0.670			2.149	0.370	0.725		
Fe1–S3A	2.259	2.120	0.370	0.687			2.149	0.370	0.743		
Fe1–SG	2.439	2.120	0.370	0.422	2.153	0.153	2.149	0.370	0.457	2.329	-0.671
Fe2–S1	2.406	2.120	0.370	0.462			2.149	0.370	0.499		
Fe2–S2A	2.272	2.120	0.370	0.663			2.149	0.370	0.717		
Fe2–S4A	2.292	2.120	0.370	0.628			2.149	0.370	0.679		
Fe2–SG	2.461	2.120	0.370	0.398	2.151	0.151	2.149	0.370	0.430	2.326	-0.674
Fe3–S2A	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe3–S3A	2.245	2.120	0.370	0.713			2.149	0.370	0.771		
Fe3–S4A	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe3–SG	2.201	2.120	0.370	0.803	2.815	0.815	2.149	0.370	0.869	3.044	0.044
Fe4–S1	2.348	2.120	0.370	0.540			2.149	0.370	0.584		
Fe4–S3A	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe4–S4A	2.278	2.120	0.370	0.652			2.149	0.370	0.706		

Fe4–SG	2.348	2.120	0.370	0.540	2.394	0.394	2.149	0.370	0.584	2.589	-0.411
Fe5–S1	2.623	2.120	0.370	0.257			2.149	0.370	0.278		
Fe5–S2B	2.126	2.120	0.370	0.984			2.149	0.370	1.064		
Fe5–S4B	2.334	2.120	0.370	0.561			2.149	0.370	0.607		
Fe5–SG	2.355	2.120	0.370	0.530	2.331	0.331	2.149	0.370	0.573	2.521	-0.479
Fe6–S1	2.513	2.120	0.370	0.346			2.149	0.370	0.374		
Fe6–S2B	2.322	2.120	0.370	0.579			2.149	0.370	0.627		
Fe6–S3B	2.162	2.120	0.370	0.893			2.149	0.370	0.965		
Fe6–SG	2.446	2.120	0.370	0.414	2.232	0.232	2.149	0.370	0.448	2.414	-0.586
Fe7–S2B	2.460	2.120	0.370	0.399			2.149	0.370	0.431		
Fe7–S3B	2.460	2.120	0.370	0.399			2.149	0.370	0.431		
Fe7–S4B	2.312	2.120	0.370	0.595			2.149	0.370	0.644		
Fe7–SG	2.407	2.120	0.370	0.460	1.853	-0.147	2.149	0.370	0.498	2.005	-0.995
Fe8–S1	2.448	2.120	0.370	0.412			2.149	0.370	0.446		
Fe8–S3B	2.237	2.120	0.370	0.729			2.149	0.370	0.788		
Fe8–S4B	2.291	2.120	0.370	0.630			2.149	0.370	0.681		
Fe8–SG	2.402	2.120	0.370	0.467	2.238	0.238	2.149	0.370	0.505	2.420	-0.580
					18.167					19.648	

Table S79 The adopted bond valence analyses for irons in P-cluster [1] from MoFe protein 6O7O which is reported as P^N at 1.89sÅ resolution.

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	2.446	2.120	0.370	0.414			2.149	0.370	0.448		
Fe1–S2A	2.282	2.120	0.370	0.645			2.149	0.370	0.698		
Fe1–S3A	2.238	2.120	0.370	0.727			2.149	0.370	0.786		
Fe1–SG	2.331	2.120	0.370	0.565	2.352	0.352	2.149	0.370	0.611	2.544	-0.456
Fe2–S1	2.430	2.120	0.370	0.433			2.149	0.370	0.468		
Fe2–S2A	2.270	2.120	0.370	0.667			2.149	0.370	0.721		
Fe2–S4A	2.301	2.120	0.370	0.613			2.149	0.370	0.663		
Fe2–SG	2.357	2.120	0.370	0.527	2.239	0.239	2.149	0.370	0.570	2.422	-0.578
Fe3–S2A	2.301	2.120	0.370	0.613			2.149	0.370	0.663		
Fe3–S3A	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe3–S4A	2.348	2.120	0.370	0.540			2.149	0.370	0.584		
Fe3–SG	2.334	2.120	0.370	0.561	2.356	0.356	2.149	0.370	0.607	2.548	-0.452
Fe4–S1	2.334	2.120	0.370	0.561			2.149	0.370	0.607		
Fe4–S3A	2.255	2.120	0.370	0.694			2.149	0.370	0.751		
Fe4–S4A	2.307	2.120	0.370	0.603			2.149	0.370	0.652		

Fe4–SG	2.336	2.120	0.370	0.558	2.416	0.416	2.149	0.370	0.603	2.613	-0.387
Fe5–S1	2.399	2.120	0.370	0.470			2.149	0.370	0.509		
Fe5–S2B	2.237	2.120	0.370	0.729			2.149	0.370	0.788		
Fe5–S4B	2.291	2.120	0.370	0.630			2.149	0.370	0.681		
Fe5–SG	2.345	2.120	0.370	0.544	2.374	0.374	2.149	0.370	0.589	2.567	-0.433
Fe6–S1	2.533	2.120	0.370	0.328			2.149	0.370	0.354		
Fe6–S2B	2.275	2.120	0.370	0.658			2.149	0.370	0.711		
Fe6–S3B	2.332	2.120	0.370	0.564			2.149	0.370	0.610		
Fe6–SG	2.279	2.120	0.370	0.651	2.200	0.200	2.149	0.370	0.704	2.379	-0.621
Fe7–S2B	2.214	2.120	0.370	0.776			2.149	0.370	0.839		
Fe7–S3B	2.330	2.120	0.370	0.567			2.149	0.370	0.613		
Fe7–S4B	2.306	2.120	0.370	0.605			2.149	0.370	0.654		
Fe7–SG	2.370	2.120	0.370	0.509	2.456	0.456	2.149	0.370	0.550	2.657	-0.343
Fe8–S1	2.397	2.120	0.370	0.473			2.149	0.370	0.512		
Fe8–S3B	2.294	2.120	0.370	0.625			2.149	0.370	0.676		
Fe8–S4B	2.335	2.120	0.370	0.559			2.149	0.370	0.605		
Fe8–SG	2.336	2.120	0.370	0.558	2.215	0.215	2.149	0.370	0.603	2.396	-0.604
					18.608					20.125	

Table S80 The adopted bond valence analyses for irons in P-cluster [2] from MoFe protein 6O7O which is reported as P^N at 1.89 Å resolution.

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	2.431	2.120	0.370	0.431			2.149	0.370	0.467		
Fe1–S2A	2.241	2.120	0.370	0.721			2.149	0.370	0.780		
Fe1–S3A	2.260	2.120	0.370	0.685			2.149	0.370	0.741		
Fe1–SG	2.393	2.120	0.370	0.478	2.316	0.316	2.149	0.370	0.517	2.504	-0.496
Fe2–S1	2.421	2.120	0.370	0.443			2.149	0.370	0.479		
Fe2–S2A	2.254	2.120	0.370	0.696			2.149	0.370	0.753		
Fe2–S4A	2.272	2.120	0.370	0.663			2.149	0.370	0.717		
Fe2–SG	2.327	2.120	0.370	0.572	2.374	0.374	2.149	0.370	0.618	2.568	-0.432
Fe3–S2A	2.302	2.120	0.370	0.611			2.149	0.370	0.661		
Fe3–S3A	2.257	2.120	0.370	0.691			2.149	0.370	0.747		
Fe3–S4A	2.309	2.120	0.370	0.600			2.149	0.370	0.649		
Fe3–SG	2.248	2.120	0.370	0.708	2.610	0.610	2.149	0.370	0.765	2.822	-0.178
Fe4–S1	2.329	2.120	0.370	0.568			2.149	0.370	0.615		
Fe4–S3A	2.260	2.120	0.370	0.685			2.149	0.370	0.741		
Fe4–S4A	2.307	2.120	0.370	0.603			2.149	0.370	0.652		

Fe4–SG	2.323	2.120	0.370	0.578	2.434	0.434	2.149	0.370	0.625	2.633	-0.367
Fe5–S1	2.417	2.120	0.370	0.448			2.149	0.370	0.485		
Fe5–S2B	2.196	2.120	0.370	0.814			2.149	0.370	0.881		
Fe5–S4B	2.313	2.120	0.370	0.594			2.149	0.370	0.642		
Fe5–SG	2.348	2.120	0.370	0.540	2.396	0.396	2.149	0.370	0.584	2.591	-0.409
Fe6–S1	2.486	2.120	0.370	0.372			2.149	0.370	0.402		
Fe6–S2B	2.303	2.120	0.370	0.610			2.149	0.370	0.660		
Fe6–S3B	2.295	2.120	0.370	0.623			2.149	0.370	0.674		
Fe6–SG	2.340	2.120	0.370	0.552	2.157	0.157	2.149	0.370	0.597	2.332	-0.668
Fe7–S2B	2.226	2.120	0.370	0.751			2.149	0.370	0.812		
Fe7–S3B	2.318	2.120	0.370	0.586			2.149	0.370	0.633		
Fe7–S4B	2.299	2.120	0.370	0.616			2.149	0.370	0.667		
Fe7–SG	2.355	2.120	0.370	0.530	2.483	0.483	2.149	0.370	0.573	2.685	-0.315
Fe8–S1	2.418	2.120	0.370	0.447			2.149	0.370	0.483		
Fe8–S3B	2.324	2.120	0.370	0.576			2.149	0.370	0.623		
Fe8–S4B	2.336	2.120	0.370	0.558			2.149	0.370	0.603		
Fe8–SG	2.254	2.120	0.370	0.696	2.277	0.277	2.149	0.370	0.753	2.463	-0.537
					19.046					20.599	

Table S81 The adopted bond valence analyses for irons in P-cluster [1] from MoFe protein 6O7P which is reported as P^N at 1.7 Å resolution.

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	2.441	2.120	0.370	0.420			2.149	0.370	0.454		
Fe1–S2A	2.271	2.120	0.370	0.665			2.149	0.370	0.719		
Fe1–S3A	2.267	2.120	0.370	0.672			2.149	0.370	0.727		
Fe1–SG	2.354	2.120	0.370	0.531	2.288	0.288	2.149	0.370	0.575	2.475	-0.525
Fe2–S1	2.405	2.120	0.370	0.463			2.149	0.370	0.501		
Fe2–S2A	2.266	2.120	0.370	0.674			2.149	0.370	0.729		
Fe2–S4A	2.279	2.120	0.370	0.651			2.149	0.370	0.704		
Fe2–SG	2.332	2.120	0.370	0.564	2.351	0.351	2.149	0.370	0.610	2.543	-0.457
Fe3–S2A	2.274	2.120	0.370	0.660			2.149	0.370	0.713		
Fe3–S3A	2.248	2.120	0.370	0.708			2.149	0.370	0.765		
Fe3–S4A	2.303	2.120	0.370	0.610			2.149	0.370	0.660		
Fe3–SG	2.249	2.120	0.370	0.706	2.683	0.683	2.149	0.370	0.763	2.901	-0.099
Fe4–S1	2.373	2.120	0.370	0.505			2.149	0.370	0.546		
Fe4–S3A	2.275	2.120	0.370	0.658			2.149	0.370	0.711		
Fe4–S4A	2.283	2.120	0.370	0.644			2.149	0.370	0.696		

Fe4–SG	2.368	2.120	0.370	0.512	2.318	0.318	2.149	0.370	0.553	2.507	-0.493
Fe5–S1	2.600	2.120	0.370	0.273			2.149	0.370	0.296		
Fe5–S2B	2.196	2.120	0.370	0.814			2.149	0.370	0.881		
Fe5–S4B	2.307	2.120	0.370	0.603			2.149	0.370	0.652		
Fe5–SG	2.204	2.120	0.370	0.797	2.488	0.488	2.149	0.370	0.862	2.691	-0.309
Fe6–S1	2.675	2.120	0.370	0.223			2.149	0.370	0.241		
Fe6–S2B	2.264	2.120	0.370	0.678			2.149	0.370	0.733		
Fe6–S3B	2.302	2.120	0.370	0.611			2.149	0.370	0.661		
Fe6–SG	2.248	2.120	0.370	0.708	2.220	0.220	2.149	0.370	0.765	2.401	-0.599
Fe7–S2B	2.261	2.120	0.370	0.683			2.149	0.370	0.739		
Fe7–S3B	2.318	2.120	0.370	0.586			2.149	0.370	0.633		
Fe7–S4B	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe7–SG	2.492	2.120	0.370	0.366	2.287	0.287	2.149	0.370	0.396	2.474	-0.526
Fe8–S1	2.375	2.120	0.370	0.502			2.149	0.370	0.543		
Fe8–S3B	2.300	2.120	0.370	0.615			2.149	0.370	0.665		
Fe8–S4B	2.312	2.120	0.370	0.595			2.149	0.370	0.644		
Fe8–SG	2.317	2.120	0.370	0.587	2.299	0.299	2.149	0.370	0.635	2.487	-0.513
					18.934					20.477	

Table S82 The adopted bond valence analyses for irons in P-cluster [2] from MoFe protein 6O7P which is reported as P^N at 1.7 Å resolution.

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	2.426	2.120	0.370	0.437			2.149	0.370	0.473		
Fe1–S2A	2.266	2.120	0.370	0.674			2.149	0.370	0.729		
Fe1–S3A	2.258	2.120	0.370	0.689			2.149	0.370	0.745		
Fe1–SG	2.337	2.120	0.370	0.556	2.356	0.356	2.149	0.370	0.602	2.548	-0.452
Fe2–S1	2.412	2.120	0.370	0.454			2.149	0.370	0.491		
Fe2–S2A	2.274	2.120	0.370	0.660			2.149	0.370	0.713		
Fe2–S4A	2.283	2.120	0.370	0.644			2.149	0.370	0.696		
Fe2–SG	2.311	2.120	0.370	0.597	2.354	0.354	2.149	0.370	0.645	2.546	-0.454
Fe3–S2A	2.268	2.120	0.370	0.670			2.149	0.370	0.725		
Fe3–S3A	2.245	2.120	0.370	0.713			2.149	0.370	0.771		
Fe3–S4A	2.303	2.120	0.370	0.610			2.149	0.370	0.660		
Fe3–SG	2.311	2.120	0.370	0.597	2.590	0.590	2.149	0.370	0.645	2.801	-0.199
Fe4–S1	2.376	2.120	0.370	0.501			2.149	0.370	0.541		
Fe4–S3A	2.276	2.120	0.370	0.656			2.149	0.370	0.709		
Fe4–S4A	2.285	2.120	0.370	0.640			2.149	0.370	0.692		

Fe4–SG	2.372	2.120	0.370	0.506	2.303	0.303	2.149	0.370	0.547	2.491	-0.509
Fe5–S1	2.517	2.120	0.370	0.342			2.149	0.370	0.370		
Fe5–S2B	2.195	2.120	0.370	0.817			2.149	0.370	0.883		
Fe5–S4B	2.307	2.120	0.370	0.603			2.149	0.370	0.652		
Fe5–SG	2.184	2.120	0.370	0.841	2.603	0.603	2.149	0.370	0.910	2.815	-0.185
Fe6–S1	2.667	2.120	0.370	0.228			2.149	0.370	0.247		
Fe6–S2B	2.268	2.120	0.370	0.670			2.149	0.370	0.725		
Fe6–S3B	2.314	2.120	0.370	0.592			2.149	0.370	0.640		
Fe6–SG	2.289	2.120	0.370	0.633	2.124	0.124	2.149	0.370	0.685	2.297	-0.703
Fe7–S2B	2.259	2.120	0.370	0.687			2.149	0.370	0.743		
Fe7–S3B	2.321	2.120	0.370	0.581			2.149	0.370	0.628		
Fe7–S4B	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe7–SG	2.528	2.120	0.370	0.332	2.236	0.236	2.149	0.370	0.359	2.419	-0.581
Fe8–S1	2.386	2.120	0.370	0.487			2.149	0.370	0.527		
Fe8–S3B	2.289	2.120	0.370	0.633			2.149	0.370	0.685		
Fe8–S4B	2.311	2.120	0.370	0.597			2.149	0.370	0.645		
Fe8–SG	2.338	2.120	0.370	0.555	2.272	0.272	2.149	0.370	0.600	2.457	-0.543
					18.839					20.375	

Table S83 The adopted bond valence analyses for irons in P-cluster [1] from MoFe protein 6O7Q which is reported as P^N at 2.0 Å resolution.

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	2.468	2.120	0.370	0.390			2.149	0.370	0.422		
Fe1–S2A	2.295	2.120	0.370	0.623			2.149	0.370	0.674		
Fe1–S3A	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe1–SG	2.406	2.120	0.370	0.462	2.117	0.117	2.149	0.370	0.499	2.290	-0.710
Fe2–S1	2.453	2.120	0.370	0.407			2.149	0.370	0.440		
Fe2–S2A	2.258	2.120	0.370	0.689			2.149	0.370	0.745		
Fe2–S4A	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe2–SG	2.399	2.120	0.370	0.470	2.227	0.227	2.149	0.370	0.509	2.409	-0.591
Fe3–S2A	2.310	2.120	0.370	0.598			2.149	0.370	0.647		
Fe3–S3A	2.294	2.120	0.370	0.625			2.149	0.370	0.676		
Fe3–S4A	2.282	2.120	0.370	0.645			2.149	0.370	0.698		
Fe3–SG	2.273	2.120	0.370	0.661	2.530	0.530	2.149	0.370	0.715	2.736	-0.264
Fe4–S1	2.405	2.120	0.370	0.463			2.149	0.370	0.501		
Fe4–S3A	2.276	2.120	0.370	0.656			2.149	0.370	0.709		
Fe4–S4A	2.315	2.120	0.370	0.590			2.149	0.370	0.638		

Fe4–SG	2.444	2.120	0.370	0.417	2.126	0.126	2.149	0.370	0.451	2.299	-0.701
Fe5–S1	2.708	2.120	0.370	0.204			2.149	0.370	0.221		
Fe5–S2B	2.178	2.120	0.370	0.855			2.149	0.370	0.925		
Fe5–S4B	2.322	2.120	0.370	0.579			2.149	0.370	0.627		
Fe5–SG	2.283	2.120	0.370	0.644	2.282	0.282	2.149	0.370	0.696	2.468	-0.532
Fe6–S1	2.945	2.120	0.370	0.108			2.149	0.370	0.116		
Fe6–S2B	2.245	2.120	0.370	0.713			2.149	0.370	0.771		
Fe6–S3B	2.336	2.120	0.370	0.558			2.149	0.370	0.603		
Fe6–SG	2.304	2.120	0.370	0.608	1.987	-0.013	2.149	0.370	0.658	2.149	-0.851
Fe7–S2B	2.256	2.120	0.370	0.692			2.149	0.370	0.749		
Fe7–S3B	2.341	2.120	0.370	0.550			2.149	0.370	0.595		
Fe7–S4B	2.279	2.120	0.370	0.651			2.149	0.370	0.704		
Fe7–SG	2.501	2.120	0.370	0.357	2.251	0.251	2.149	0.370	0.386	2.434	-0.566
Fe8–S1	2.395	2.120	0.370	0.476			2.149	0.370	0.514		
Fe8–S3B	2.259	2.120	0.370	0.687			2.149	0.370	0.743		
Fe8–S4B	2.336	2.120	0.370	0.558			2.149	0.370	0.603		
Fe8–SG	2.287	2.120	0.370	0.637	2.357	0.357	2.149	0.370	0.689	2.549	-0.451
					17.876					19.334	

Table S84 The adopted bond valence analyses for irons in P-cluster [2] from MoFe protein 6O7Q which is reported as P^N at 2.0 Å resolution.

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	2.453	2.120	0.370	0.407			2.149	0.370	0.440		
Fe1–S2A	2.310	2.120	0.370	0.598			2.149	0.370	0.647		
Fe1–S3A	2.270	2.120	0.370	0.667			2.149	0.370	0.721		
Fe1–SG	2.459	2.120	0.370	0.400	2.072	0.072	2.149	0.370	0.433	2.241	-0.759
Fe2–S1	2.456	2.120	0.370	0.403			2.149	0.370	0.436		
Fe2–S2A	2.247	2.120	0.370	0.709			2.149	0.370	0.767		
Fe2–S4A	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe2–SG	2.365	2.120	0.370	0.516	2.269	0.269	2.149	0.370	0.558	2.454	-0.546
Fe3–S2A	2.262	2.120	0.370	0.681			2.149	0.370	0.737		
Fe3–S3A	2.266	2.120	0.370	0.674			2.149	0.370	0.729		
Fe3–S4A	2.290	2.120	0.370	0.632			2.149	0.370	0.683		
Fe3–SG	2.317	2.120	0.370	0.587	2.574	0.574	2.149	0.370	0.635	2.784	-0.216
Fe4–S1	2.392	2.120	0.370	0.479			2.149	0.370	0.519		
Fe4–S3A	2.245	2.120	0.370	0.713			2.149	0.370	0.771		
Fe4–S4A	2.298	2.120	0.370	0.618			2.149	0.370	0.669		

Fe4–SG	2.423	2.120	0.370	0.441	2.252	0.252	2.149	0.370	0.477	2.435	-0.565
Fe5–S1	2.724	2.120	0.370	0.195			2.149	0.370	0.211		
Fe5–S2B	2.185	2.120	0.370	0.839			2.149	0.370	0.907		
Fe5–S4B	2.294	2.120	0.370	0.625			2.149	0.370	0.676		
Fe5–SG	2.264	2.120	0.370	0.678	2.337	0.337	2.149	0.370	0.733	2.527	-0.473
Fe6–S1	2.953	2.120	0.370	0.105			2.149	0.370	0.114		
Fe6–S2B	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe6–S3B	2.292	2.120	0.370	0.628			2.149	0.370	0.679		
Fe6–SG	2.421	2.120	0.370	0.443	1.838	-0.162	2.149	0.370	0.479	1.988	-1.012
Fe7–S2B	2.239	2.120	0.370	0.725			2.149	0.370	0.784		
Fe7–S3B	2.359	2.120	0.370	0.524			2.149	0.370	0.567		
Fe7–S4B	2.310	2.120	0.370	0.598			2.149	0.370	0.647		
Fe7–SG	2.434	2.120	0.370	0.428	2.276	0.276	2.149	0.370	0.463	2.461	-0.539
Fe8–S1	2.393	2.120	0.370	0.478			2.149	0.370	0.517		
Fe8–S3B	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe8–S4B	2.302	2.120	0.370	0.611			2.149	0.370	0.661		
Fe8–SG	2.346	2.120	0.370	0.543	2.285	0.285	2.149	0.370	0.587	2.471	-0.529
					17.902					19.361	

Table S85 The adopted bond valence analyses for irons in P-cluster [1] from MoFe protein 6O7R which is reported as P^N at 2.27 Å resolution.

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	2.460	2.120	0.370	0.399			2.149	0.370	0.431		
Fe1–S2A	2.248	2.120	0.370	0.708			2.149	0.370	0.765		
Fe1–S3A	2.185	2.120	0.370	0.839			2.149	0.370	0.907		
Fe1–SG	2.493	2.120	0.370	0.365	2.310	0.310	2.149	0.370	0.395	2.499	-0.501
Fe2–S1	2.382	2.120	0.370	0.493			2.149	0.370	0.533		
Fe2–S2A	2.245	2.120	0.370	0.713			2.149	0.370	0.771		
Fe2–S4A	2.246	2.120	0.370	0.711			2.149	0.370	0.769		
Fe2–SG	2.377	2.120	0.370	0.499	2.417	0.417	2.149	0.370	0.540	2.614	-0.386
Fe3–S2A	2.259	2.120	0.370	0.687			2.149	0.370	0.743		
Fe3–S3A	2.267	2.120	0.370	0.672			2.149	0.370	0.727		
Fe3–S4A	2.259	2.120	0.370	0.687			2.149	0.370	0.743		
Fe3–SG	2.251	2.120	0.370	0.702	2.748	0.748	2.149	0.370	0.759	2.972	-0.028
Fe4–S1	2.351	2.120	0.370	0.536			2.149	0.370	0.579		
Fe4–S3A	2.207	2.120	0.370	0.790			2.149	0.370	0.855		
Fe4–S4A	2.261	2.120	0.370	0.683			2.149	0.370	0.739		

Fe4–SG	2.414	2.120	0.370	0.452	2.461	0.461	2.149	0.370	0.489	2.662	-0.338
Fe5–S1	2.839	2.120	0.370	0.143			2.149	0.370	0.155		
Fe5–S2B	2.157	2.120	0.370	0.905			2.149	0.370	0.979		
Fe5–S4B	2.276	2.120	0.370	0.656			2.149	0.370	0.709		
Fe5–SG	2.241	2.120	0.370	0.721	2.425	0.425	2.149	0.370	0.780	2.623	-0.377
Fe6–S1	2.981	2.120	0.370	0.098			2.149	0.370	0.106		
Fe6–S2B	2.283	2.120	0.370	0.644			2.149	0.370	0.696		
Fe6–S3B	2.289	2.120	0.370	0.633			2.149	0.370	0.685		
Fe6–SG	2.222	2.120	0.370	0.759	2.134	0.134	2.149	0.370	0.821	2.308	-0.692
Fe7–S2B	2.232	2.120	0.370	0.739			2.149	0.370	0.799		
Fe7–S3B	2.256	2.120	0.370	0.692			2.149	0.370	0.749		
Fe7–S4B	2.291	2.120	0.370	0.630			2.149	0.370	0.681		
Fe7–SG	2.586	2.120	0.370	0.284	2.345	0.345	2.149	0.370	0.307	2.536	-0.464
Fe8–S1	2.347	2.120	0.370	0.541			2.149	0.370	0.586		
Fe8–S3B	2.233	2.120	0.370	0.737			2.149	0.370	0.797		
Fe8–S4B	2.251	2.120	0.370	0.702			2.149	0.370	0.759		
Fe8–SG	2.273	2.120	0.370	0.661	2.641	0.641	2.149	0.370	0.715	2.857	-0.143
					19.481					21.069	

Table S86 The adopted bond valence analyses for irons in P-cluster [2] from MoFe protein 6O7R which is reported as P^N at 2.27 Å resolution.

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	2.456	2.120	0.370	0.403			2.149	0.370	0.436		
Fe1–S2A	2.242	2.120	0.370	0.719			2.149	0.370	0.778		
Fe1–S3A	2.221	2.120	0.370	0.761			2.149	0.370	0.823		
Fe1–SG	2.401	2.120	0.370	0.468	2.351	0.351	2.149	0.370	0.506	2.543	-0.457
Fe2–S1	2.392	2.120	0.370	0.479			2.149	0.370	0.519		
Fe2–S2A	2.230	2.120	0.370	0.743			2.149	0.370	0.803		
Fe2–S4A	2.257	2.120	0.370	0.691			2.149	0.370	0.747		
Fe2–SG	2.341	2.120	0.370	0.550	2.463	0.463	2.149	0.370	0.595	2.664	-0.336
Fe3–S2A	2.241	2.120	0.370	0.721			2.149	0.370	0.780		
Fe3–S3A	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe3–S4A	2.260	2.120	0.370	0.685			2.149	0.370	0.741		
Fe3–SG	2.234	2.120	0.370	0.735	2.783	0.783	2.149	0.370	0.795	3.010	0.010
Fe4–S1	2.355	2.120	0.370	0.530			2.149	0.370	0.573		
Fe4–S3A	2.199	2.120	0.370	0.808			2.149	0.370	0.874		
Fe4–S4A	2.233	2.120	0.370	0.737			2.149	0.370	0.797		

Fe4–SG	2.420	2.120	0.370	0.444	2.519	0.519	2.149	0.370	0.481	2.724	-0.276
Fe5–S1	2.856	2.120	0.370	0.137			2.149	0.370	0.148		
Fe5–S2B	2.152	2.120	0.370	0.917			2.149	0.370	0.992		
Fe5–S4B	2.246	2.120	0.370	0.711			2.149	0.370	0.769		
Fe5–SG	2.234	2.120	0.370	0.735	2.500	0.500	2.149	0.370	0.795	2.704	-0.296
Fe6–S1	3.027	2.120	0.370	0.086			2.149	0.370	0.093		
Fe6–S2B	2.256	2.120	0.370	0.692			2.149	0.370	0.749		
Fe6–S3B	2.318	2.120	0.370	0.586			2.149	0.370	0.633		
Fe6–SG	2.217	2.120	0.370	0.769	2.134	0.134	2.149	0.370	0.832	2.308	-0.692
Fe7–S2B	2.235	2.120	0.370	0.733			2.149	0.370	0.793		
Fe7–S3B	2.249	2.120	0.370	0.706			2.149	0.370	0.763		
Fe7–S4B	2.279	2.120	0.370	0.651			2.149	0.370	0.704		
Fe7–SG	2.655	2.120	0.370	0.236	2.325	0.325	2.149	0.370	0.255	2.514	-0.486
Fe8–S1	2.302	2.120	0.370	0.611			2.149	0.370	0.661		
Fe8–S3B	2.251	2.120	0.370	0.702			2.149	0.370	0.759		
Fe8–S4B	2.257	2.120	0.370	0.691			2.149	0.370	0.747		
Fe8–SG	2.281	2.120	0.370	0.647	2.651	0.651	2.149	0.370	0.700	2.867	-0.133
					19.726					21.334	

Table S87 The adopted bond valence analyses for irons in P-cluster [1] from MoFe protein 6OP3 which is reported as P^N at 1.6 Å resolution.

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	2.431	2.120	0.370	0.431			2.149	0.370	0.467		
Fe1–S2A	2.168	2.120	0.370	0.878			2.149	0.370	0.950		
Fe1–S3A	2.210	2.120	0.370	0.784			2.149	0.370	0.848		
Fe1–SG	2.351	2.120	0.370	0.536	2.630	0.630	2.149	0.370	0.579	2.844	-0.156
Fe2–S1	2.447	2.120	0.370	0.413			2.149	0.370	0.447		
Fe2–S2A	2.197	2.120	0.370	0.812			2.149	0.370	0.878		
Fe2–S4A	2.183	2.120	0.370	0.843			2.149	0.370	0.912		
Fe2–SG	2.385	2.120	0.370	0.489	2.557	0.557	2.149	0.370	0.528	2.766	-0.234
Fe3–S2A	2.241	2.120	0.370	0.721			2.149	0.370	0.780		
Fe3–S3A	2.301	2.120	0.370	0.613			2.149	0.370	0.663		
Fe3–S4A	2.196	2.120	0.370	0.814			2.149	0.370	0.881		
Fe3–SG	2.321	2.120	0.370	0.581	2.729	0.729	2.149	0.370	0.628	2.952	-0.048
Fe4–S1	2.350	2.120	0.370	0.537			2.149	0.370	0.581		
Fe4–S3A	2.203	2.120	0.370	0.799			2.149	0.370	0.864		
Fe4–S4A	2.200	2.120	0.370	0.806			2.149	0.370	0.871		

Fe4–SG	2.371	2.120	0.370	0.507	2.649	0.649	2.149	0.370	0.549	2.865	-0.135
Fe5–S1	2.415	2.120	0.370	0.451			2.149	0.370	0.487		
Fe5–S2B	2.321	2.120	0.370	0.581			2.149	0.370	0.628		
Fe5–S4B	2.310	2.120	0.370	0.598			2.149	0.370	0.647		
Fe5–SG	2.324	2.120	0.370	0.576	2.206	0.206	2.149	0.370	0.623	2.386	-0.614
Fe6–S1	2.493	2.120	0.370	0.365			2.149	0.370	0.395		
Fe6–S2B	2.345	2.120	0.370	0.544			2.149	0.370	0.589		
Fe6–S3B	2.313	2.120	0.370	0.594			2.149	0.370	0.642		
Fe6–SG	2.325	2.120	0.370	0.575	2.077	0.077	2.149	0.370	0.621	2.247	-0.753
Fe7–S2B	2.353	2.120	0.370	0.533			2.149	0.370	0.576		
Fe7–S3B	2.351	2.120	0.370	0.536			2.149	0.370	0.579		
Fe7–S4B	2.355	2.120	0.370	0.530			2.149	0.370	0.573		
Fe7–SG	2.363	2.120	0.370	0.519	2.117	0.117	2.149	0.370	0.561	2.289	-0.711
Fe8–S1	2.421	2.120	0.370	0.443			2.149	0.370	0.479		
Fe8–S3B	2.289	2.120	0.370	0.633			2.149	0.370	0.685		
Fe8–S4B	2.303	2.120	0.370	0.610			2.149	0.370	0.660		
Fe8–SG	2.316	2.120	0.370	0.589	2.275	0.275	2.149	0.370	0.637	2.461	-0.539
					19.241					20.810	

Table S88 The adopted bond valence analyses for irons in P-cluster [2] from MoFe protein 6OP3 which is reported as P^N at 1.6 Å resolution.

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	2.444	2.120	0.370	0.417			2.149	0.370	0.451		
Fe1–S2A	2.251	2.120	0.370	0.702			2.149	0.370	0.759		
Fe1–S3A	2.180	2.120	0.370	0.850			2.149	0.370	0.920		
Fe1–SG	2.352	2.120	0.370	0.534	2.503	0.503	2.149	0.370	0.578	2.707	-0.293
Fe2–S1	2.450	2.120	0.370	0.410			2.149	0.370	0.443		
Fe2–S2A	2.244	2.120	0.370	0.715			2.149	0.370	0.774		
Fe2–S4A	2.181	2.120	0.370	0.848			2.149	0.370	0.917		
Fe2–SG	2.395	2.120	0.370	0.476	2.449	0.449	2.149	0.370	0.514	2.648	-0.352
Fe3–S2A	2.203	2.120	0.370	0.799			2.149	0.370	0.864		
Fe3–S3A	2.325	2.120	0.370	0.575			2.149	0.370	0.621		
Fe3–S4A	2.219	2.120	0.370	0.765			2.149	0.370	0.828		
Fe3–SG	2.324	2.120	0.370	0.576	2.715	0.715	2.149	0.370	0.623	2.936	-0.064
Fe4–S1	2.355	2.120	0.370	0.530			2.149	0.370	0.573		
Fe4–S3A	2.170	2.120	0.370	0.874			2.149	0.370	0.945		
Fe4–S4A	2.180	2.120	0.370	0.850			2.149	0.370	0.920		

Fe4–SG	2.388	2.120	0.370	0.485	2.738	0.738	2.149	0.370	0.524	2.962	-0.038
Fe5–S1	2.414	2.120	0.370	0.452			2.149	0.370	0.489		
Fe5–S2B	2.303	2.120	0.370	0.610			2.149	0.370	0.660		
Fe5–S4B	2.292	2.120	0.370	0.628			2.149	0.370	0.679		
Fe5–SG	2.351	2.120	0.370	0.536	2.225	0.225	2.149	0.370	0.579	2.407	-0.593
Fe6–S1	2.478	2.120	0.370	0.380			2.149	0.370	0.411		
Fe6–S2B	2.355	2.120	0.370	0.530			2.149	0.370	0.573		
Fe6–S3B	2.324	2.120	0.370	0.576			2.149	0.370	0.623		
Fe6–SG	2.302	2.120	0.370	0.611	2.098	0.098	2.149	0.370	0.661	2.269	-0.731
Fe7–S2B	2.354	2.120	0.370	0.531			2.149	0.370	0.575		
Fe7–S3B	2.343	2.120	0.370	0.547			2.149	0.370	0.592		
Fe7–S4B	2.317	2.120	0.370	0.587			2.149	0.370	0.635		
Fe7–SG	2.354	2.120	0.370	0.531	2.197	0.197	2.149	0.370	0.575	2.376	-0.624
Fe8–S1	2.421	2.120	0.370	0.443			2.149	0.370	0.479		
Fe8–S3B	2.318	2.120	0.370	0.586			2.149	0.370	0.633		
Fe8–S4B	2.266	2.120	0.370	0.674			2.149	0.370	0.729		
Fe8–SG	2.321	2.120	0.370	0.581	2.284	0.284	2.149	0.370	0.628	2.470	-0.530
					19.209					20.775	

Table S89 The adopted bond valence analyses for irons in P-cluster [1] from MoFe protein 6VXT which is reported as P^N at 1.74 Å resolution.

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	2.407	2.120	0.370	0.460			2.149	0.370	0.498		
Fe1–S2A	2.304	2.120	0.370	0.608			2.149	0.370	0.658		
Fe1–S3A	2.259	2.120	0.370	0.687			2.149	0.370	0.743		
Fe1–SG	2.419	2.120	0.370	0.446	2.201	0.201	2.149	0.370	0.482	2.381	-0.619
Fe2–S1	2.481	2.120	0.370	0.377			2.149	0.370	0.408		
Fe2–S2A	2.291	2.120	0.370	0.630			2.149	0.370	0.681		
Fe2–S4A	2.292	2.120	0.370	0.628			2.149	0.370	0.679		
Fe2–SG	2.440	2.120	0.370	0.421	2.056	0.056	2.149	0.370	0.455	2.224	-0.776
Fe3–S2A	2.332	2.120	0.370	0.564			2.149	0.370	0.610		
Fe3–S3A	2.348	2.120	0.370	0.540			2.149	0.370	0.584		
Fe3–S4A	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe3–SG	2.374	2.120	0.370	0.503	2.244	0.244	2.149	0.370	0.544	2.427	-0.573
Fe4–S1	2.372	2.120	0.370	0.506			2.149	0.370	0.547		
Fe4–S3A	2.235	2.120	0.370	0.733			2.149	0.370	0.793		
Fe4–S4A	2.250	2.120	0.370	0.704			2.149	0.370	0.761		

Fe4–SG	2.448	2.120	0.370	0.412	2.355	0.355	2.149	0.370	0.446	2.547	-0.453
Fe5–S1	2.423	2.120	0.370	0.441			2.149	0.370	0.477		
Fe5–S2B	2.309	2.120	0.370	0.600			2.149	0.370	0.649		
Fe5–S4B	2.235	2.120	0.370	0.733			2.149	0.370	0.793		
Fe5–SG	2.364	2.120	0.370	0.517	2.291	0.291	2.149	0.370	0.559	2.478	-0.522
Fe6–S1	2.503	2.120	0.370	0.355			2.149	0.370	0.384		
Fe6–S2B	2.337	2.120	0.370	0.556			2.149	0.370	0.602		
Fe6–S3B	2.307	2.120	0.370	0.603			2.149	0.370	0.652		
Fe6–SG	2.413	2.120	0.370	0.453	1.968	-0.032	2.149	0.370	0.490	2.128	-0.872
Fe7–S2B	2.344	2.120	0.370	0.546			2.149	0.370	0.590		
Fe7–S3B	2.360	2.120	0.370	0.523			2.149	0.370	0.565		
Fe7–S4B	2.354	2.120	0.370	0.531			2.149	0.370	0.575		
Fe7–SG	2.521	2.120	0.370	0.338	1.938	-0.062	2.149	0.370	0.366	2.096	-0.904
Fe8–S1	2.443	2.120	0.370	0.418			2.149	0.370	0.452		
Fe8–S3B	2.361	2.120	0.370	0.521			2.149	0.370	0.564		
Fe8–S4B	2.248	2.120	0.370	0.708			2.149	0.370	0.765		
Fe8–SG	2.463	2.120	0.370	0.396	2.042	0.042	2.149	0.370	0.428	2.209	-0.791
					17.095					18.489	

Table S90 The adopted bond valence analyses for irons in P-cluster [2] from MoFe protein 6VXT which is reported as P^N at 1.74 Å resolution.

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	2.428	2.120	0.370	0.435			2.149	0.370	0.470		
Fe1–S2A	2.323	2.120	0.370	0.578			2.149	0.370	0.625		
Fe1–S3A	2.193	2.120	0.370	0.821			2.149	0.370	0.888		
Fe1–SG	2.373	2.120	0.370	0.505	2.338	0.338	2.149	0.370	0.546	2.529	-0.471
Fe2–S1	2.492	2.120	0.370	0.366			2.149	0.370	0.396		
Fe2–S2A	2.292	2.120	0.370	0.628			2.149	0.370	0.679		
Fe2–S4A	2.291	2.120	0.370	0.630			2.149	0.370	0.681		
Fe2–SG	2.408	2.120	0.370	0.459	2.083	0.083	2.149	0.370	0.497	2.253	-0.747
Fe3–S2A	2.331	2.120	0.370	0.565			2.149	0.370	0.611		
Fe3–S3A	2.372	2.120	0.370	0.506			2.149	0.370	0.547		
Fe3–S4A	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe3–SG	2.471	2.120	0.370	0.387	2.101	0.101	2.149	0.370	0.419	2.272	-0.728
Fe4–S1	2.365	2.120	0.370	0.516			2.149	0.370	0.558		
Fe4–S3A	2.249	2.120	0.370	0.706			2.149	0.370	0.763		
Fe4–S4A	2.262	2.120	0.370	0.681			2.149	0.370	0.737		

Fe4–SG	2.455	2.120	0.370	0.404	2.307	0.307	2.149	0.370	0.437	2.495	-0.505
Fe5–S1	2.425	2.120	0.370	0.439			2.149	0.370	0.474		
Fe5–S2B	2.307	2.120	0.370	0.603			2.149	0.370	0.652		
Fe5–S4B	2.253	2.120	0.370	0.698			2.149	0.370	0.755		
Fe5–SG	2.317	2.120	0.370	0.587	2.327	0.327	2.149	0.370	0.635	2.517	-0.483
Fe6–S1	2.511	2.120	0.370	0.348			2.149	0.370	0.376		
Fe6–S2B	2.321	2.120	0.370	0.581			2.149	0.370	0.628		
Fe6–S3B	2.308	2.120	0.370	0.602			2.149	0.370	0.651		
Fe6–SG	2.433	2.120	0.370	0.429	1.959	-0.041	2.149	0.370	0.464	2.119	-0.881
Fe7–S2B	2.327	2.120	0.370	0.572			2.149	0.370	0.618		
Fe7–S3B	2.356	2.120	0.370	0.528			2.149	0.370	0.572		
Fe7–S4B	2.352	2.120	0.370	0.534			2.149	0.370	0.578		
Fe7–SG	2.426	2.120	0.370	0.437	2.071	0.071	2.149	0.370	0.473	2.240	-0.760
Fe8–S1	2.450	2.120	0.370	0.410			2.149	0.370	0.443		
Fe8–S3B	2.358	2.120	0.370	0.526			2.149	0.370	0.568		
Fe8–S4B	2.248	2.120	0.370	0.708			2.149	0.370	0.765		
Fe8–SG	2.491	2.120	0.370	0.367	2.010	0.010	2.149	0.370	0.397	2.174	-0.826
					17.197					18.599	

Table S91 The adopted bond valence analyses for irons in P-cluster [1] from MoFe protein 7JRF which is reported as P^N at 1.33 Å resolution.

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	2.473	2.120	0.370	0.385			2.149	0.370	0.417		
Fe1–S2A	2.309	2.120	0.370	0.600			2.149	0.370	0.649		
Fe1–S3A	2.256	2.120	0.370	0.692			2.149	0.370	0.749		
Fe1–SG	2.361	2.120	0.370	0.521	2.199	0.199	2.149	0.370	0.564	2.378	-0.622
Fe2–S1	2.440	2.120	0.370	0.421			2.149	0.370	0.455		
Fe2–S2A	2.323	2.120	0.370	0.578			2.149	0.370	0.625		
Fe2–S4A	2.311	2.120	0.370	0.597			2.149	0.370	0.645		
Fe2–SG	2.294	2.120	0.370	0.625	2.220	0.220	2.149	0.370	0.676	2.401	-0.599
Fe3–S2A	2.304	2.120	0.370	0.608			2.149	0.370	0.658		
Fe3–S3A	2.268	2.120	0.370	0.670			2.149	0.370	0.725		
Fe3–S4A	2.332	2.120	0.370	0.564			2.149	0.370	0.610		
Fe3–SG	2.306	2.120	0.370	0.605	2.447	0.447	2.149	0.370	0.654	2.647	-0.353
Fe4–S1	2.390	2.120	0.370	0.482			2.149	0.370	0.521		
Fe4–S3A	2.271	2.120	0.370	0.665			2.149	0.370	0.719		
Fe4–S4A	2.288	2.120	0.370	0.635			2.149	0.370	0.687		
Fe4–SG	2.340	2.120	0.370	0.552	2.334	0.334	2.149	0.370	0.597	2.524	-0.476

Fe5–S1	2.431	2.120	0.370	0.431			2.149	0.370	0.467		
Fe5–S2B	2.323	2.120	0.370	0.578			2.149	0.370	0.625		
Fe5–S4B	2.305	2.120	0.370	0.607			2.149	0.370	0.656		
Fe5–SG	2.379	2.120	0.370	0.497	2.112	0.112	2.149	0.370	0.537	2.285	-0.715
Fe6–S1	2.460	2.120	0.370	0.399			2.149	0.370	0.431		
Fe6–S2B	2.347	2.120	0.370	0.541			2.149	0.370	0.586		
Fe6–S3B	2.329	2.120	0.370	0.568			2.149	0.370	0.615		
Fe6–SG	2.318	2.120	0.370	0.586	2.094	0.094	2.149	0.370	0.633	2.265	-0.735
Fe7–S2B	2.361	2.120	0.370	0.521			2.149	0.370	0.564		
Fe7–S3B	2.326	2.120	0.370	0.573			2.149	0.370	0.620		
Fe7–S4B	2.341	2.120	0.370	0.550			2.149	0.370	0.595		
Fe7–SG	2.328	2.120	0.370	0.570	2.215	0.215	2.149	0.370	0.616	2.395	-0.605
Fe8–S1	2.452	2.120	0.370	0.408			2.149	0.370	0.441		
Fe8–S3B	2.304	2.120	0.370	0.608			2.149	0.370	0.658		
Fe8–S4B	2.272	2.120	0.370	0.663			2.149	0.370	0.717		
Fe8–SG	2.322	2.120	0.370	0.579	2.258	0.258	2.149	0.370	0.627	2.442	-0.558
					17.880					19.338	

Table S92 The adopted bond valence analyses for irons in P-cluster [2] from MoFe protein 7JRF which is reported as P^N at 1.33 Å resolution.

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	2.490	2.120	0.370	0.368			2.149	0.370	0.398		
Fe1–S2A	2.301	2.120	0.370	0.613			2.149	0.370	0.663		
Fe1–S3A	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe1–SG	2.353	2.120	0.370	0.533	2.175	0.175	2.149	0.370	0.576	2.352	-0.648
Fe2–S1	2.441	2.120	0.370	0.420			2.149	0.370	0.454		
Fe2–S2A	2.334	2.120	0.370	0.561			2.149	0.370	0.607		
Fe2–S4A	2.299	2.120	0.370	0.616			2.149	0.370	0.667		
Fe2–SG	2.310	2.120	0.370	0.598	2.196	0.196	2.149	0.370	0.647	2.375	-0.625
Fe3–S2A	2.307	2.120	0.370	0.603			2.149	0.370	0.652		
Fe3–S3A	2.253	2.120	0.370	0.698			2.149	0.370	0.755		
Fe3–S4A	2.346	2.120	0.370	0.543			2.149	0.370	0.587		
Fe3–SG	2.312	2.120	0.370	0.595	2.439	0.439	2.149	0.370	0.644	2.638	-0.362
Fe4–S1	2.396	2.120	0.370	0.474			2.149	0.370	0.513		
Fe4–S3A	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe4–S4A	2.272	2.120	0.370	0.663			2.149	0.370	0.717		

Fe4–SG	2.331	2.120	0.370	0.565	2.355	0.355	2.149	0.370	0.611	2.547	-0.453
Fe5–S1	2.429	2.120	0.370	0.434			2.149	0.370	0.469		
Fe5–S2B	2.336	2.120	0.370	0.558			2.149	0.370	0.603		
Fe5–S4B	2.283	2.120	0.370	0.644			2.149	0.370	0.696		
Fe5–SG	2.365	2.120	0.370	0.516	2.151	0.151	2.149	0.370	0.558	2.326	-0.674
Fe6–S1	2.462	2.120	0.370	0.397			2.149	0.370	0.429		
Fe6–S2B	2.360	2.120	0.370	0.523			2.149	0.370	0.565		
Fe6–S3B	2.313	2.120	0.370	0.594			2.149	0.370	0.642		
Fe6–SG	2.317	2.120	0.370	0.587	2.100	0.100	2.149	0.370	0.635	2.272	-0.728
Fe7–S2B	2.376	2.120	0.370	0.501			2.149	0.370	0.541		
Fe7–S3B	2.327	2.120	0.370	0.572			2.149	0.370	0.618		
Fe7–S4B	2.345	2.120	0.370	0.544			2.149	0.370	0.589		
Fe7–SG	2.319	2.120	0.370	0.584	2.201	0.201	2.149	0.370	0.632	2.380	-0.620
Fe8–S1	2.447	2.120	0.370	0.413			2.149	0.370	0.447		
Fe8–S3B	2.325	2.120	0.370	0.575			2.149	0.370	0.621		
Fe8–S4B	2.268	2.120	0.370	0.670			2.149	0.370	0.725		
Fe8–SG	2.301	2.120	0.370	0.613	2.271	0.271	2.149	0.370	0.663	2.456	-0.544
					17.888					19.347	

Table S93 The adopted bond valence analyses for irons in P-cluster [1] from VFe protein 5N6Y which is reported as P^N at 1.35 Å resolution.

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	2.443	2.120	0.370	0.418			2.149	0.370	0.452		
Fe1–S2A	2.299	2.120	0.370	0.616			2.149	0.370	0.667		
Fe1–S3A	2.277	2.120	0.370	0.654			2.149	0.370	0.708		
Fe1–SG	2.334	2.120	0.370	0.561	2.249	0.249	2.149	0.370	0.607	2.433	-0.567
Fe2–S1	2.486	2.120	0.370	0.372			2.149	0.370	0.402		
Fe2–S2A	2.268	2.120	0.370	0.670			2.149	0.370	0.725		
Fe2–S4A	2.288	2.120	0.370	0.635			2.149	0.370	0.687		
Fe2–SG	2.401	2.120	0.370	0.468	2.145	0.145	2.149	0.370	0.506	2.320	-0.680
Fe3–S2A	2.321	2.120	0.370	0.581			2.149	0.370	0.628		
Fe3–S3A	2.319	2.120	0.370	0.584			2.149	0.370	0.632		
Fe3–S4A	2.275	2.120	0.370	0.658			2.149	0.370	0.711		
Fe3–SG	2.303	2.120	0.370	0.610	2.432	0.432	2.149	0.370	0.660	2.631	-0.369
Fe4–S1	2.421	2.120	0.370	0.443			2.149	0.370	0.479		
Fe4–S3A	2.251	2.120	0.370	0.702			2.149	0.370	0.759		
Fe4–S4A	2.273	2.120	0.370	0.661			2.149	0.370	0.715		

Fe4–SG	2.364	2.120	0.370	0.517	2.324	0.324	2.149	0.370	0.559	2.513	-0.487
Fe5–S1	2.465	2.120	0.370	0.394			2.149	0.370	0.426		
Fe5–S2B	2.252	2.120	0.370	0.700			2.149	0.370	0.757		
Fe5–S4B	2.262	2.120	0.370	0.681			2.149	0.370	0.737		
Fe5–SG	2.358	2.120	0.370	0.526	2.300	0.300	2.149	0.370	0.568	2.488	-0.512
Fe6–S1	2.527	2.120	0.370	0.333			2.149	0.370	0.360		
Fe6–S2B	2.344	2.120	0.370	0.546			2.149	0.370	0.590		
Fe6–S3B	2.304	2.120	0.370	0.608			2.149	0.370	0.658		
Fe6–SG	2.258	2.120	0.370	0.689	2.176	0.176	2.149	0.370	0.745	2.353	-0.647
Fe7–S2B	2.313	2.120	0.370	0.594			2.149	0.370	0.642		
Fe7–S3B	2.297	2.120	0.370	0.620			2.149	0.370	0.670		
Fe7–S4B	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe7–SG	2.276	2.120	0.370	0.656	2.511	0.511	2.149	0.370	0.709	2.716	-0.284
Fe8–S1	2.397	2.120	0.370	0.473			2.149	0.370	0.512		
Fe8–S3B	2.249	2.120	0.370	0.706			2.149	0.370	0.763		
Fe8–S4B	2.275	2.120	0.370	0.658			2.149	0.370	0.711		
Fe8–SG	2.294	2.120	0.370	0.625	2.461	0.461	2.149	0.370	0.676	2.662	-0.338
					18.599					20.115	

Table S94 The adopted bond valence analyses for irons in P-cluster [2] from VFe protein 5N6Y which is reported as P^N at 1.35 Å resolution.

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	2.459	2.120	0.370	0.400			2.149	0.370	0.433		
Fe1–S2A	2.300	2.120	0.370	0.615			2.149	0.370	0.665		
Fe1–S3A	2.313	2.120	0.370	0.594			2.149	0.370	0.642		
Fe1–SG	2.319	2.120	0.370	0.584	2.192	0.192	2.149	0.370	0.632	2.371	-0.629
Fe2–S1	2.493	2.120	0.370	0.365			2.149	0.370	0.395		
Fe2–S2A	2.295	2.120	0.370	0.623			2.149	0.370	0.674		
Fe2–S4A	2.302	2.120	0.370	0.611			2.149	0.370	0.661		
Fe2–SG	2.331	2.120	0.370	0.565	2.165	0.165	2.149	0.370	0.611	2.341	-0.659
Fe3–S2A	2.318	2.120	0.370	0.586			2.149	0.370	0.633		
Fe3–S3A	2.351	2.120	0.370	0.536			2.149	0.370	0.579		
Fe3–S4A	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe3–SG	2.323	2.120	0.370	0.578	2.336	0.336	2.149	0.370	0.625	2.526	-0.474
Fe4–S1	2.421	2.120	0.370	0.443			2.149	0.370	0.479		
Fe4–S3A	2.293	2.120	0.370	0.627			2.149	0.370	0.678		
Fe4–S4A	2.289	2.120	0.370	0.633			2.149	0.370	0.685		

Fe4–SG	2.331	2.120	0.370	0.565	2.269	0.269	2.149	0.370	0.611	2.453	-0.547
Fe5–S1	2.453	2.120	0.370	0.407			2.149	0.370	0.440		
Fe5–S2B	2.290	2.120	0.370	0.632			2.149	0.370	0.683		
Fe5–S4B	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe5–SG	2.318	2.120	0.370	0.586	2.261	0.261	2.149	0.370	0.633	2.445	-0.555
Fe6–S1	2.552	2.120	0.370	0.311			2.149	0.370	0.336		
Fe6–S2B	2.339	2.120	0.370	0.553			2.149	0.370	0.598		
Fe6–S3B	2.310	2.120	0.370	0.598			2.149	0.370	0.647		
Fe6–SG	2.278	2.120	0.370	0.652	2.115	0.115	2.149	0.370	0.706	2.288	-0.712
Fe7–S2B	2.315	2.120	0.370	0.590			2.149	0.370	0.638		
Fe7–S3B	2.293	2.120	0.370	0.627			2.149	0.370	0.678		
Fe7–S4B	2.289	2.120	0.370	0.633			2.149	0.370	0.685		
Fe7–SG	2.310	2.120	0.370	0.598	2.449	0.449	2.149	0.370	0.647	2.648	-0.352
Fe8–S1	2.398	2.120	0.370	0.472			2.149	0.370	0.510		
Fe8–S3B	2.279	2.120	0.370	0.651			2.149	0.370	0.704		
Fe8–S4B	2.265	2.120	0.370	0.676			2.149	0.370	0.731		
Fe8–SG	2.290	2.120	0.370	0.632	2.430	0.430	2.149	0.370	0.683	2.628	-0.372
					18.216					19.701	

Table S95 The adopted bond valence analyses for irons in P^N [1] from VFe protein 6FEA which was reported as superposition of $P^N/^{1+}$ at 1.2 Å resolution.

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	2.425	2.120	0.370	0.439			2.149	0.370	0.474		
Fe1–S2A	2.332	2.120	0.370	0.564			2.149	0.370	0.610		
Fe1–S4A	2.312	2.120	0.370	0.595			2.149	0.370	0.644		
Fe1–SG	2.336	2.120	0.370	0.558	2.155	0.155	2.149	0.370	0.603	2.331	-0.669
Fe2–S1	2.485	2.120	0.370	0.373			2.149	0.370	0.403		
Fe2–S2A	2.301	2.120	0.370	0.613			2.149	0.370	0.663		
Fe2–S3A	2.292	2.120	0.370	0.628			2.149	0.370	0.679		
Fe2–SG	2.385	2.120	0.370	0.489	2.103	0.103	2.149	0.370	0.528	2.274	-0.726
Fe3–S2A	2.345	2.120	0.370	0.544			2.149	0.370	0.589		
Fe3–S3A	2.337	2.120	0.370	0.556			2.149	0.370	0.602		
Fe3–S4A	2.288	2.120	0.370	0.635			2.149	0.370	0.687		
Fe3–SG	2.304	2.120	0.370	0.608	2.344	0.344	2.149	0.370	0.658	2.535	-0.465
Fe4–S1	2.413	2.120	0.370	0.453			2.149	0.370	0.490		
Fe4–S3A	2.292	2.120	0.370	0.628			2.149	0.370	0.679		
Fe4–S4A	2.268	2.120	0.370	0.670			2.149	0.370	0.725		

Fe4–SG	2.329	2.120	0.370	0.568	2.320	0.320	2.149	0.370	0.615	2.509	-0.491
Fe5–S1	2.464	2.120	0.370	0.395			2.149	0.370	0.427		
Fe5–S2B	2.286	2.120	0.370	0.638			2.149	0.370	0.691		
Fe5–S4B	2.288	2.120	0.370	0.635			2.149	0.370	0.687		
Fe5–SG	2.345	2.120	0.370	0.544	2.213	0.213	2.149	0.370	0.589	2.393	-0.607
Fe6–S1(P^N)	2.439	2.120	0.370	0.422			2.149	0.370	0.457		
Fe6–S2B(P^N)	2.403	2.120	0.370	0.465			2.149	0.370	0.503		
Fe6–S3B(P^N)	2.356	2.120	0.370	0.528			2.149	0.370	0.572		
Fe6–SG(P^N)	2.291	2.120	0.370	0.630	2.046 (P^N)	0.046	2.149	0.370	0.681	2.213 (P^N)	-0.787
Fe7–S2B	2.329	2.120	0.370	0.568			2.149	0.370	0.615		
Fe7–S3B	2.301	2.120	0.370	0.613			2.149	0.370	0.663		
Fe7–S4B	2.288	2.120	0.370	0.635			2.149	0.370	0.687		
Fe7–SG	2.296	2.120	0.370	0.621	2.438	0.438	2.149	0.370	0.672	2.637	-0.363
Fe8–S1	2.423	2.120	0.370	0.441			2.149	0.370	0.477		
Fe8–S3B	2.279	2.120	0.370	0.651			2.149	0.370	0.704		
Fe8–S4B	2.262	2.120	0.370	0.681			2.149	0.370	0.737		
Fe8–SG	2.286	2.120	0.370	0.638	2.411	0.411	2.149	0.370	0.691	2.608	-0.392
					18.030 (P^N)					19.500 (P^N)	

Table S96 The adopted bond valence analyses for irons in P^N [2] from VFe protein 6FEA which was reported as superposition of $P^N/^{1+}$ at 1.2 Å resolution.

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	2.438	2.120	0.370	0.423			2.149	0.370	0.458		
Fe1–S2A	2.317	2.120	0.370	0.587			2.149	0.370	0.635		
Fe1–S4A	2.305	2.120	0.370	0.607			2.149	0.370	0.656		
Fe1–SG	2.332	2.120	0.370	0.564	2.181	0.181	2.149	0.370	0.610	2.359	-0.641
Fe2–S1	2.497	2.120	0.370	0.361			2.149	0.370	0.390		
Fe2–S2A	2.289	2.120	0.370	0.633			2.149	0.370	0.685		
Fe2–S3A	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe2–SG	2.397	2.120	0.370	0.473	2.108	0.108	2.149	0.370	0.512	2.279	-0.721
Fe3–S2A	2.314	2.120	0.370	0.592			2.149	0.370	0.640		
Fe3–S3A	2.340	2.120	0.370	0.552			2.149	0.370	0.597		
Fe3–S4A	2.294	2.120	0.370	0.625			2.149	0.370	0.676		
Fe3–SG	2.300	2.120	0.370	0.615	2.383	0.383	2.149	0.370	0.665	2.578	-0.422
Fe4–S1	2.412	2.120	0.370	0.454			2.149	0.370	0.491		
Fe4–S3A	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe4–S4A	2.272	2.120	0.370	0.663			2.149	0.370	0.717		

Fe4–SG	2.350	2.120	0.370	0.537	2.295	0.295	2.149	0.370	0.581	2.482	-0.518
Fe5–S1	2.452	2.120	0.370	0.408			2.149	0.370	0.441		
Fe5–S2B	2.290	2.120	0.370	0.632			2.149	0.370	0.683		
Fe5–S4B	2.270	2.120	0.370	0.667			2.149	0.370	0.721		
Fe5–SG	2.343	2.120	0.370	0.547	2.253	0.253	2.149	0.370	0.592	2.437	-0.563
Fe6–S1(P^N)	2.426	2.120	0.370	0.437			2.149	0.370	0.473		
Fe6–S2B(P^N)	2.393	2.120	0.370	0.478			2.149	0.370	0.517		
Fe6–S3B(P^N)	2.346	2.120	0.370	0.543			2.149	0.370	0.587		
Fe6–SG(P^N)	2.301	2.120	0.370	0.613	2.072 (P^N)	0.072	2.149	0.370	0.663	2.240 (P^N)	-0.760
Fe7–S2B	2.328	2.120	0.370	0.570			2.149	0.370	0.616		
Fe7–S3B	2.298	2.120	0.370	0.618			2.149	0.370	0.669		
Fe7–S4B	2.281	2.120	0.370	0.647			2.149	0.370	0.700		
Fe7–SG	2.296	2.120	0.370	0.621	2.457	0.457	2.149	0.370	0.672	2.657	-0.343
Fe8–S1	2.423	2.120	0.370	0.441			2.149	0.370	0.477		
Fe8–S3B	2.267	2.120	0.370	0.672			2.149	0.370	0.727		
Fe8–S4B	2.268	2.120	0.370	0.670			2.149	0.370	0.725		
Fe8–SG	2.299	2.120	0.370	0.616	2.400	0.400	2.149	0.370	0.667	2.595	-0.405
					18.148 (P^N)					19.627 (P^N)	

Table S97 The adopted bond valence analyses for irons in P^N [1] from VFe protein 7ADR which was reported as superposition of $P^{N}/^{1+}$ at 1.0 Å resolution.

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	2.432	2.120	0.370	0.430			2.149	0.370	0.465		
Fe1–S2A	2.336	2.120	0.370	0.558			2.149	0.370	0.603		
Fe1–S3A	2.308	2.120	0.370	0.602			2.149	0.370	0.651		
Fe1–SG	2.332	2.120	0.370	0.564	2.154	0.154	2.149	0.370	0.610	2.329	-0.671
Fe2–S1	2.483	2.120	0.370	0.375			2.149	0.370	0.405		
Fe2–S2A	2.298	2.120	0.370	0.618			2.149	0.370	0.669		
Fe2–S4A	2.306	2.120	0.370	0.605			2.149	0.370	0.654		
Fe2–SG	2.386	2.120	0.370	0.487	2.085	0.085	2.149	0.370	0.527	2.255	-0.745
Fe3–S2A	2.340	2.120	0.370	0.552			2.149	0.370	0.597		
Fe3–S3A	2.341	2.120	0.370	0.550			2.149	0.370	0.595		
Fe3–S4A	2.295	2.120	0.370	0.623			2.149	0.370	0.674		
Fe3–SG	2.310	2.120	0.370	0.598	2.324	0.324	2.149	0.370	0.647	2.513	-0.487
Fe4–S1	2.420	2.120	0.370	0.444			2.149	0.370	0.481		
Fe4–S3A	2.289	2.120	0.370	0.633			2.149	0.370	0.685		
Fe4–S4A	2.278	2.120	0.370	0.652			2.149	0.370	0.706		

Fe4–SG	2.335	2.120	0.370	0.559	2.290	0.290	2.149	0.370	0.605	2.476	-0.524
Fe5–S1	2.468	2.120	0.370	0.390			2.149	0.370	0.422		
Fe5–S2B	2.298	2.120	0.370	0.618			2.149	0.370	0.669		
Fe5–S4B	2.292	2.120	0.370	0.628			2.149	0.370	0.679		
Fe5–SG	2.344	2.120	0.370	0.546	2.183	0.183	2.149	0.370	0.590	2.361	-0.639
Fe6–S1(P^N)	2.436	2.120	0.370	0.426			2.149	0.370	0.460		
Fe6–S2B(P^N)	2.421	2.120	0.370	0.443			2.149	0.370	0.479		
Fe6–S3B(P^N)	2.381	2.120	0.370	0.494			2.149	0.370	0.534		
Fe6–SG(P^N)	2.259	2.120	0.370	0.687	2.050	0.050	2.149	0.370	0.743	2.217	-0.783
Fe7–S2B	2.332	2.120	0.370	0.564			2.149	0.370	0.610		
Fe7–S3B	2.307	2.120	0.370	0.603			2.149	0.370	0.652		
Fe7–S4B	2.304	2.120	0.370	0.608			2.149	0.370	0.658		
Fe7–SG	2.296	2.120	0.370	0.621	2.397	0.397	2.149	0.370	0.672	2.592	-0.408
Fe8–S1	2.428	2.120	0.370	0.435			2.149	0.370	0.470		
Fe8–S3B	2.279	2.120	0.370	0.651			2.149	0.370	0.704		
Fe8–S4B	2.279	2.120	0.370	0.651			2.149	0.370	0.704		
Fe8–SG	2.292	2.120	0.370	0.628	2.365	0.365	2.149	0.370	0.679	2.557	-0.443
					17.846 (P^N)					19.301 (P^N)	

Table S98 The adopted bond valence analyses for irons in P^N [2] from VFe protein 7ADR which was reported as superposition of $P^N/^{1+}$ at 1.0 Å resolution.

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	2.434	2.120	0.370	0.428			2.149	0.370	0.463		
Fe1–S2A	2.339	2.120	0.370	0.553			2.149	0.370	0.598		
Fe1–S3A	2.310	2.120	0.370	0.598			2.149	0.370	0.647		
Fe1–SG	2.336	2.120	0.370	0.558	2.137	0.137	2.149	0.370	0.603	2.312	-0.688
Fe2–S1	2.484	2.120	0.370	0.374			2.149	0.370	0.404		
Fe2–S2A	2.300	2.120	0.370	0.615			2.149	0.370	0.665		
Fe2–S4A	2.307	2.120	0.370	0.603			2.149	0.370	0.652		
Fe2–SG	2.385	2.120	0.370	0.489	2.081	0.081	2.149	0.370	0.528	2.250	-0.750
Fe3–S2A	2.348	2.120	0.370	0.540			2.149	0.370	0.584		
Fe3–S3A	2.333	2.120	0.370	0.562			2.149	0.370	0.608		
Fe3–S4A	2.305	2.120	0.370	0.607			2.149	0.370	0.656		
Fe3–SG	2.305	2.120	0.370	0.607	2.315	0.315	2.149	0.370	0.656	2.504	-0.496
Fe4–S1	2.421	2.120	0.370	0.443			2.149	0.370	0.479		
Fe4–S3A	2.292	2.120	0.370	0.628			2.149	0.370	0.679		
Fe4–S4A	2.285	2.120	0.370	0.640			2.149	0.370	0.692		

Fe4–SG	2.339	2.120	0.370	0.553	2.265	0.265	2.149	0.370	0.598	2.450	-0.550
Fe5–S1	2.459	2.120	0.370	0.400			2.149	0.370	0.433		
Fe5–S2B	2.297	2.120	0.370	0.620			2.149	0.370	0.670		
Fe5–S4B	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe5–SG	2.343	2.120	0.370	0.547	2.204	0.204	2.149	0.370	0.592	2.384	-0.616
Fe6–S1(P^N)	2.433	2.120	0.370	0.429			2.149	0.370	0.464		
Fe6–S2B(P^N)	2.410	2.120	0.370	0.457			2.149	0.370	0.494		
Fe6–S3B(P^N)	2.326	2.120	0.370	0.573			2.149	0.370	0.620		
Fe6–SG(P^N)	2.294	2.120	0.370	0.625	2.084	0.084	2.149	0.370	0.676	2.254	-0.746
Fe7–S2B	2.329	2.120	0.370	0.568			2.149	0.370	0.615		
Fe7–S3B	2.307	2.120	0.370	0.603			2.149	0.370	0.652		
Fe7–S4B	2.304	2.120	0.370	0.608			2.149	0.370	0.658		
Fe7–SG	2.294	2.120	0.370	0.625	2.405	0.405	2.149	0.370	0.676	2.601	-0.399
Fe8–S1	2.425	2.120	0.370	0.439			2.149	0.370	0.474		
Fe8–S3B	2.280	2.120	0.370	0.649			2.149	0.370	0.702		
Fe8–S4B	2.276	2.120	0.370	0.656			2.149	0.370	0.709		
Fe8–SG	2.292	2.120	0.370	0.628	2.372	0.372	2.149	0.370	0.679	2.565	-0.435
					17.862 (P^N)					19.319 (P^N)	

Table S99 The adopted bond valence analyses for irons in P^N [1] from VFe protein 7ADY which was reported as superposition of $P^{N}/^{1+}$ at 1.05 Å resolution.

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	2.434	2.120	0.370	0.428			2.149	0.370	0.463		
Fe1–S2A	2.322	2.120	0.370	0.579			2.149	0.370	0.627		
Fe1–S3A	2.318	2.120	0.370	0.586			2.149	0.370	0.633		
Fe1–SG	2.348	2.120	0.370	0.540	2.133	0.133	2.149	0.370	0.584	2.307	-0.693
Fe2–S1	2.487	2.120	0.370	0.371			2.149	0.370	0.401		
Fe2–S2A	2.300	2.120	0.370	0.615			2.149	0.370	0.665		
Fe2–S4A	2.308	2.120	0.370	0.602			2.149	0.370	0.651		
Fe2–SG	2.386	2.120	0.370	0.487	2.075	0.075	2.149	0.370	0.527	2.244	-0.756
Fe3–S2A	2.341	2.120	0.370	0.550			2.149	0.370	0.595		
Fe3–S3A	2.342	2.120	0.370	0.549			2.149	0.370	0.594		
Fe3–S4A	2.303	2.120	0.370	0.610			2.149	0.370	0.660		
Fe3–SG	2.303	2.120	0.370	0.610	2.319	0.319	2.149	0.370	0.660	2.508	-0.492
Fe4–S1	2.427	2.120	0.370	0.436			2.149	0.370	0.472		
Fe4–S3A	2.293	2.120	0.370	0.627			2.149	0.370	0.678		
Fe4–S4A	2.284	2.120	0.370	0.642			2.149	0.370	0.694		

Fe4–SG	2.341	2.120	0.370	0.550	2.255	0.255	2.149	0.370	0.595	2.439	-0.561
Fe5–S1	2.463	2.120	0.370	0.396			2.149	0.370	0.428		
Fe5–S2B	2.298	2.120	0.370	0.618			2.149	0.370	0.669		
Fe5–S4B	2.295	2.120	0.370	0.623			2.149	0.370	0.674		
Fe5–SG	2.350	2.120	0.370	0.537	2.174	0.174	2.149	0.370	0.581	2.351	-0.649
Fe6–S1(P^N)	2.422	2.120	0.370	0.442			2.149	0.370	0.478		
Fe6–S2B(P^N)	2.412	2.120	0.370	0.454			2.149	0.370	0.491		
Fe6–S3B(P^N)	2.326	2.120	0.370	0.573			2.149	0.370	0.620		
Fe6–SG(P^N)	2.300	2.120	0.370	0.615	2.084	0.084	2.149	0.370	0.665	2.254	-0.746
Fe7–S2B	2.333	2.120	0.370	0.562			2.149	0.370	0.608		
Fe7–S3B	2.296	2.120	0.370	0.621			2.149	0.370	0.672		
Fe7–S4B	2.299	2.120	0.370	0.616			2.149	0.370	0.667		
Fe7–SG	2.301	2.120	0.370	0.613	2.413	0.413	2.149	0.370	0.663	2.610	-0.390
Fe8–S1	2.435	2.120	0.370	0.427			2.149	0.370	0.462		
Fe8–S3B	2.268	2.120	0.370	0.670			2.149	0.370	0.725		
Fe8–S4B	2.291	2.120	0.370	0.630			2.149	0.370	0.681		
Fe8–SG	2.300	2.120	0.370	0.615	2.342	0.342	2.149	0.370	0.665	2.533	-0.467
					17.795 (P^N)					19.245 (P^N)	

Table S100 The adopted bond valence analyses for irons in P^N [2] from VFe protein 7ADY which was reported as superposition of $P^{N}/^{1+}$ at 1.05 Å resolution.

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	2.421	2.120	0.370	0.443			2.149	0.370	0.479		
Fe1–S2A	2.331	2.120	0.370	0.565			2.149	0.370	0.611		
Fe1–S3A	2.314	2.120	0.370	0.592			2.149	0.370	0.640		
Fe1–SG	2.337	2.120	0.370	0.556	2.157	0.157	2.149	0.370	0.602	2.333	-0.667
Fe2–S1	2.479	2.120	0.370	0.379			2.149	0.370	0.410		
Fe2–S2A	2.302	2.120	0.370	0.611			2.149	0.370	0.661		
Fe2–S4A	2.309	2.120	0.370	0.600			2.149	0.370	0.649		
Fe2–SG	2.387	2.120	0.370	0.486	2.076	0.076	2.149	0.370	0.526	2.246	-0.754
Fe3–S2A	2.343	2.120	0.370	0.547			2.149	0.370	0.592		
Fe3–S3A	2.342	2.120	0.370	0.549			2.149	0.370	0.594		
Fe3–S4A	2.299	2.120	0.370	0.616			2.149	0.370	0.667		
Fe3–SG	2.300	2.120	0.370	0.615	2.327	0.327	2.149	0.370	0.665	2.517	-0.483
Fe4–S1	2.414	2.120	0.370	0.452			2.149	0.370	0.489		
Fe4–S3A	2.297	2.120	0.370	0.620			2.149	0.370	0.670		
Fe4–S4A	2.278	2.120	0.370	0.652			2.149	0.370	0.706		

Fe4–SG	2.333	2.120	0.370	0.562	2.286	0.286	2.149	0.370	0.608	2.473	-0.527
Fe5–S1	2.473	2.120	0.370	0.385			2.149	0.370	0.417		
Fe5–S2B	2.288	2.120	0.370	0.635			2.149	0.370	0.687		
Fe5–S4B	2.291	2.120	0.370	0.630			2.149	0.370	0.681		
Fe5–SG	2.361	2.120	0.370	0.521	2.171	0.171	2.149	0.370	0.564	2.349	-0.651
Fe6–S1(P^N)	2.430	2.120	0.370	0.433			2.149	0.370	0.468		
Fe6–S2B(P^N)	2.413	2.120	0.370	0.453			2.149	0.370	0.490		
Fe6–S3B(P^N)	2.379	2.120	0.370	0.497			2.149	0.370	0.537		
Fe6–SG(P^N)	2.285	2.120	0.370	0.640	2.022	0.022	2.149	0.370	0.692	2.187	-0.813
Fe7–S2B	2.339	2.120	0.370	0.553			2.149	0.370	0.598		
Fe7–S3B	2.306	2.120	0.370	0.605			2.149	0.370	0.654		
Fe7–S4B	2.298	2.120	0.370	0.618			2.149	0.370	0.669		
Fe7–SG	2.303	2.120	0.370	0.610	2.386	0.386	2.149	0.370	0.660	2.581	-0.419
Fe8–S1	2.442	2.120	0.370	0.419			2.149	0.370	0.453		
Fe8–S3B	2.264	2.120	0.370	0.678			2.149	0.370	0.733		
Fe8–S4B	2.288	2.120	0.370	0.635			2.149	0.370	0.687		
Fe8–SG	2.294	2.120	0.370	0.625	2.356	0.356	2.149	0.370	0.676	2.548	-0.452
					17.783 (P^N)					19.233 (P^N)	

Table S101 The adopted bond valence analyses for irons in P^N [1] from VFe protein 7AIZ which was reported as superposition of $P^{N}/^{1+}$ at 1.05 Å resolution.

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	2.431	2.120	0.370	0.431			2.149	0.370	0.467		
Fe1–S2A	2.334	2.120	0.370	0.561			2.149	0.370	0.607		
Fe1–S3A	2.318	2.120	0.370	0.586			2.149	0.370	0.633		
Fe1–SG	2.330	2.120	0.370	0.567	2.145	0.145	2.149	0.370	0.613	2.320	-0.680
Fe2–S1	2.471	2.120	0.370	0.387			2.149	0.370	0.419		
Fe2–S2A	2.298	2.120	0.370	0.618			2.149	0.370	0.669		
Fe2–S4A	2.304	2.120	0.370	0.608			2.149	0.370	0.658		
Fe2–SG	2.401	2.120	0.370	0.468	2.081	0.081	2.149	0.370	0.506	2.251	-0.749
Fe3–S2A	2.331	2.120	0.370	0.565			2.149	0.370	0.611		
Fe3–S3A	2.341	2.120	0.370	0.550			2.149	0.370	0.595		
Fe3–S4A	2.308	2.120	0.370	0.602			2.149	0.370	0.651		
Fe3–SG	2.313	2.120	0.370	0.594	2.311	0.311	2.149	0.370	0.642	2.499	-0.501
Fe4–S1	2.418	2.120	0.370	0.447			2.149	0.370	0.483		
Fe4–S3A	2.301	2.120	0.370	0.613			2.149	0.370	0.663		
Fe4–S4A	2.284	2.120	0.370	0.642			2.149	0.370	0.694		

Fe4–SG	2.330	2.120	0.370	0.567	2.269	0.269	2.149	0.370	0.613	2.454	-0.546
Fe5–S1	2.467	2.120	0.370	0.391			2.149	0.370	0.423		
Fe5–S2B	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe5–S4B	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe5–SG	2.356	2.120	0.370	0.528	2.202	0.202	2.149	0.370	0.572	2.382	-0.618
Fe6–S1(P^N)	2.464	2.120	0.370	0.395			2.149	0.370	0.427		
Fe6–S2B(P^N)	2.396	2.120	0.370	0.474			2.149	0.370	0.513		
Fe6–S3B(P^N)	2.308	2.120	0.370	0.602			2.149	0.370	0.651		
Fe6–SG(P^N)	2.303	2.120	0.370	0.610	2.080	0.080	2.149	0.370	0.660	2.250	-0.750
Fe7–S2B	2.326	2.120	0.370	0.573			2.149	0.370	0.620		
Fe7–S3B	2.295	2.120	0.370	0.623			2.149	0.370	0.674		
Fe7–S4B	2.299	2.120	0.370	0.616			2.149	0.370	0.667		
Fe7–SG	2.303	2.120	0.370	0.610	2.422	0.422	2.149	0.370	0.660	2.620	-0.380
Fe8–S1	2.431	2.120	0.370	0.431			2.149	0.370	0.467		
Fe8–S3B	2.262	2.120	0.370	0.681			2.149	0.370	0.737		
Fe8–S4B	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe8–SG	2.311	2.120	0.370	0.597	2.351	0.351	2.149	0.370	0.645	2.543	-0.457
					17.862 (P^N)					19.319 (P^N)	

Table S102 The adopted bond valence analyses for irons in P^N [2] from VFe protein 7AIZ which was reported as superposition of $P^{N}/^{1+}$ at 1.05 Å resolution.

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	2.415	2.120	0.370	0.451			2.149	0.370	0.487		
Fe1–S2A	2.326	2.120	0.370	0.573			2.149	0.370	0.620		
Fe1–S3A	2.314	2.120	0.370	0.592			2.149	0.370	0.640		
Fe1–SG	2.335	2.120	0.370	0.559	2.175	0.175	2.149	0.370	0.605	2.352	-0.648
Fe2–S1	2.473	2.120	0.370	0.385			2.149	0.370	0.417		
Fe2–S2A	2.302	2.120	0.370	0.611			2.149	0.370	0.661		
Fe2–S4A	2.314	2.120	0.370	0.592			2.149	0.370	0.640		
Fe2–SG	2.391	2.120	0.370	0.481	2.069	0.069	2.149	0.370	0.520	2.238	-0.762
Fe3–S2A	2.347	2.120	0.370	0.541			2.149	0.370	0.586		
Fe3–S3A	2.339	2.120	0.370	0.553			2.149	0.370	0.598		
Fe3–S4A	2.303	2.120	0.370	0.610			2.149	0.370	0.660		
Fe3–SG	2.311	2.120	0.370	0.597	2.301	0.301	2.149	0.370	0.645	2.489	-0.511
Fe4–S1	2.418	2.120	0.370	0.447			2.149	0.370	0.483		
Fe4–S3A	2.290	2.120	0.370	0.632			2.149	0.370	0.683		
Fe4–S4A	2.276	2.120	0.370	0.656			2.149	0.370	0.709		

Fe4–SG	2.334	2.120	0.370	0.561	2.295	0.295	2.149	0.370	0.607	2.482	-0.518
Fe5–S1	2.484	2.120	0.370	0.374			2.149	0.370	0.404		
Fe5–S2B	2.298	2.120	0.370	0.618			2.149	0.370	0.669		
Fe5–S4B	2.291	2.120	0.370	0.630			2.149	0.370	0.681		
Fe5–SG	2.361	2.120	0.370	0.521	2.143	0.143	2.149	0.370	0.564	2.318	-0.682
Fe6–S1(P^N)	2.463	2.120	0.370	0.396			2.149	0.370	0.428		
Fe6–S2B(P^N)	2.392	2.120	0.370	0.479			2.149	0.370	0.519		
Fe6–S3B(P^N)	2.369	2.120	0.370	0.510			2.149	0.370	0.552		
Fe6–SG(P^N)	2.306	2.120	0.370	0.605	1.990	-0.010	2.149	0.370	0.654	2.153	-0.847
Fe7–S2B	2.328	2.120	0.370	0.570			2.149	0.370	0.616		
Fe7–S3B	2.310	2.120	0.370	0.598			2.149	0.370	0.647		
Fe7–S4B	2.298	2.120	0.370	0.618			2.149	0.370	0.669		
Fe7–SG	2.304	2.120	0.370	0.608	2.395	0.395	2.149	0.370	0.658	2.590	-0.410
Fe8–S1	2.449	2.120	0.370	0.411			2.149	0.370	0.444		
Fe8–S3B	2.282	2.120	0.370	0.645			2.149	0.370	0.698		
Fe8–S4B	2.283	2.120	0.370	0.644			2.149	0.370	0.696		
Fe8–SG	2.294	2.120	0.370	0.625	2.325	0.325	2.149	0.370	0.676	2.514	-0.486
					17.694 (P^N)					19.137 (P^N)	

Table S103 The bond valence analyses of irons in P^N model compounds DUGNEZ.

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–N1	1.927	1.769	0.370	0.652			2.149	0.370	0.498		
Fe1–S2	2.269	2.120	0.370	0.669			2.149	0.370	0.658		
Fe1–S3	2.284	2.120	0.370	0.642			2.149	0.370	0.743		
Fe1–S4	2.307	2.120	0.370	0.603	2.566	0.566	2.149	0.370	0.482	2.381	-0.619
Fe2–N2	2.048	1.769	0.370	0.470			2.149	0.370	0.408		
Fe2–S1	2.415	2.120	0.370	0.451			2.149	0.370	0.681		
Fe2–S2	2.287	2.120	0.370	0.637			2.149	0.370	0.679		
Fe2–S3	2.274	2.120	0.370	0.660	2.217	0.217	2.149	0.370	0.455	2.224	-0.776
Fe3–N4	2.083	1.769	0.370	0.428			2.149	0.370	0.610		
Fe3–S1	2.390	2.120	0.370	0.482			2.149	0.370	0.584		
Fe3–S2	2.274	2.120	0.370	0.660			2.149	0.370	0.689		
Fe3–S4	2.283	2.120	0.370	0.644	2.213	0.213	2.149	0.370	0.544	2.427	-0.573
Fe4-C25	2.127	1.470	0.370	0.169			2.149	0.370	0.547		
Fe4–S1	2.381	2.120	0.370	0.494			2.149	0.370	0.793		
Fe4–S3	2.277	2.120	0.370	0.654			2.149	0.370	0.761		

Fe4–S4	2.293	2.120	0.370	0.627	1.944	-0.056	2.149	0.370	0.446	2.547	-0.453
Fe5–N3	1.917	1.769	0.370	0.670			2.149	0.370	0.477		
Fe5–S5	2.270	2.120	0.370	0.667			2.149	0.370	0.649		
Fe5–S6	2.292	2.120	0.370	0.628			2.149	0.370	0.793		
Fe5–S7	2.299	2.120	0.370	0.616	2.582	0.582	2.149	0.370	0.559	2.478	-0.522
Fe6–N4	2.055	1.769	0.370	0.462			2.149	0.370	0.384		
Fe6–S1	2.421	2.120	0.370	0.443			2.149	0.370	0.602		
Fe6–S5	2.288	2.120	0.370	0.635			2.149	0.370	0.652		
Fe6–S6	2.276	2.120	0.370	0.656	2.196	0.196	2.149	0.370	0.490	2.128	-0.872
Fe7–N2	2.059	1.769	0.370	0.457			2.149	0.370	0.590		
Fe7–S1	2.388	2.120	0.370	0.485			2.149	0.370	0.565		
Fe7–S5	2.276	2.120	0.370	0.656			2.149	0.370	0.575		
Fe7–S7	2.282	2.120	0.370	0.645	2.243	0.243	2.149	0.370	0.366	2.096	-0.904
Fe8-C45	2.111	1.470	0.370	0.177			2.149	0.370	0.452		
Fe8–S1	2.396	2.120	0.370	0.474			2.149	0.370	0.564		
Fe8–S6	2.283	2.120	0.370	0.644			2.149	0.370	0.765		
Fe8–S7	2.291	2.120	0.370	0.630	1.925	-0.075	2.149	0.370	0.428	2.209	-0.791
					17.886					19.755	

Table S104 The bond valence analyses of irons in P^N model compounds MUFPOT.

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–N1	1.934	1.769	0.370	0.640			1.815	0.370	0.725		
Fe1–S2	2.257	2.120	0.370	0.691			2.149	0.370	0.747		
Fe1–S3	2.290	2.120	0.370	0.632			2.149	0.370	0.683		
Fe1–S4	2.303	2.120	0.370	0.610	2.572	0.572	2.149	0.370	0.660	2.814	-0.186
Fe2–N2	2.080	1.769	0.370	0.431			1.815	0.370	0.489		
Fe2–S1	2.372	2.120	0.370	0.506			2.149	0.370	0.547		
Fe2–S2	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe2–S4	2.288	2.120	0.370	0.635	2.234	0.234	2.149	0.370	0.687	2.438	-0.562
Fe3–N4	2.050	1.769	0.370	0.468			1.815	0.370	0.530		
Fe3–S1	2.423	2.120	0.370	0.441			2.149	0.370	0.477		
Fe3–S2	2.294	2.120	0.370	0.625			2.149	0.370	0.676		
Fe3–S3	2.302	2.120	0.370	0.611	2.145	0.145	2.149	0.370	0.661	2.344	-0.656
Fe4–S1	2.404	2.120	0.370	0.464			2.149	0.370	0.502		
Fe4–S3	2.270	2.120	0.370	0.667			2.149	0.370	0.721		
Fe4–S4	2.295	2.120	0.370	0.623			2.149	0.370	0.674		

Fe4–S8	2.275	2.120	0.370	0.658	2.412	0.412	2.149	0.370	0.711	2.608	-0.392
Fe5–N3	1.905	1.769	0.370	0.692			1.815	0.370	0.784		
Fe5–S5	2.280	2.120	0.370	0.649			2.149	0.370	0.702		
Fe5–S6	2.302	2.120	0.370	0.611			2.149	0.370	0.661		
Fe5–S7	2.284	2.120	0.370	0.642	2.595	0.595	2.149	0.370	0.694	2.842	-0.158
Fe6–N4	2.068	1.769	0.370	0.446			1.815	0.370	0.505		
Fe6–S1	2.394	2.120	0.370	0.477			2.149	0.370	0.516		
Fe6–S5	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe6–S7	2.271	2.120	0.370	0.665	2.249	0.249	2.149	0.370	0.719	2.455	-0.545
Fe7–N2	2.083	1.769	0.370	0.428			1.815	0.370	0.485		
Fe7–S1	2.422	2.120	0.370	0.442			2.149	0.370	0.478		
Fe7–S5	2.282	2.120	0.370	0.645			2.149	0.370	0.698		
Fe7–S6	2.294	2.120	0.370	0.625	2.140	0.140	2.149	0.370	0.676	2.337	-0.663
Fe8–S1	2.405	2.120	0.370	0.463			2.149	0.370	0.501		
Fe8–S6	2.288	2.120	0.370	0.635			2.149	0.370	0.687		
Fe8–S7	2.272	2.120	0.370	0.663			2.149	0.370	0.717		
Fe8–S9	2.280	2.120	0.370	0.649	2.410	0.410	2.149	0.370	0.702	2.606	-0.394
					18.757					20.444	

Table S105 The bond valence analyses of irons in P^N model compounds MUFPUZ.

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–N1	1.918	1.769	0.370	0.669			1.815	0.370	0.757		
Fe1–S2	2.276	2.120	0.370	0.656			2.149	0.370	0.709		
Fe1–S3	2.300	2.120	0.370	0.615			2.149	0.370	0.665		
Fe1–S4	2.296	2.120	0.370	0.621	2.561	0.561	2.149	0.370	0.672	2.804	-0.196
Fe2–N2	2.064	1.769	0.370	0.451			1.815	0.370	0.510		
Fe2–S1	2.396	2.120	0.370	0.474			2.149	0.370	0.513		
Fe2–S2	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe2–S4	2.279	2.120	0.370	0.651	2.217	0.217	2.149	0.370	0.704	2.421	-0.579
Fe3–N2A	2.058	1.769	0.370	0.458			1.815	0.370	0.519		
Fe3–S1	2.424	2.120	0.370	0.440			2.149	0.370	0.476		
Fe3–S2	2.295	2.120	0.370	0.623			2.149	0.370	0.674		
Fe3–S4	2.294	2.120	0.370	0.625	2.146	0.146	2.149	0.370	0.676	2.344	-0.656
Fe4–S1	2.395	2.120	0.370	0.476			2.149	0.370	0.514		
Fe4–S3	2.304	2.120	0.370	0.608			2.149	0.370	0.658		
Fe4–S4	2.284	2.120	0.370	0.642			2.149	0.370	0.694		

Fe4–S8	2.311	2.120	0.370	0.597	2.322	0.322	2.149	0.370	0.645	2.512	-0.488
Fe1A–N1A	1.918	1.769	0.370	0.669			1.815	0.370	0.757		
Fe1A–S2A	2.276	2.120	0.370	0.656			2.149	0.370	0.709		
Fe1A–S3A	2.300	2.120	0.370	0.615			2.149	0.370	0.665		
Fe1A–S4A	2.296	2.120	0.370	0.621	2.561	0.561	2.149	0.370	0.672	2.804	-0.196
Fe2A–N2A	2.064	1.769	0.370	0.451			1.815	0.370	0.510		
Fe2A–S1	2.396	2.120	0.370	0.474			2.149	0.370	0.513		
Fe2A–S2A	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe2A–S3A	2.279	2.120	0.370	0.651	2.217	0.217	2.149	0.370	0.704	2.421	-0.579
Fe3A–N2	2.058	1.769	0.370	0.458			1.815	0.370	0.519		
Fe3A–S1	2.424	2.120	0.370	0.440			2.149	0.370	0.476		
Fe3A–S2A	2.295	2.120	0.370	0.623			2.149	0.370	0.674		
Fe3A–S4A	2.294	2.120	0.370	0.625	2.146	0.146	2.149	0.370	0.676	2.344	-0.656
Fe4A–S1	2.395	2.120	0.370	0.476			2.149	0.370	0.514		
Fe4A–S3A	2.304	2.120	0.370	0.608			2.149	0.370	0.658		
Fe4A–S4A	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe4A–S5A	2.311	2.120	0.370	0.597	2.322	0.322	2.149	0.370	0.645	2.512	-0.488
					18.493					20.161	

Table S106 The bond valence analyses of irons in P^N model compounds MUFQAG.

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–N1	1.923	1.769	0.370	0.660			1.815	0.370	0.747		
Fe1–S2	2.277	2.120	0.370	0.654			2.149	0.370	0.708		
Fe1–S3	2.289	2.120	0.370	0.633			2.149	0.370	0.685		
Fe1–S4	2.295	2.120	0.370	0.623	2.570	0.570	2.149	0.370	0.674	2.813	-0.187
Fe2–N2	2.055	1.769	0.370	0.462			1.815	0.370	0.523		
Fe2–S1	2.426	2.120	0.370	0.437			2.149	0.370	0.473		
Fe2–S2	2.291	2.120	0.370	0.630			2.149	0.370	0.681		
Fe2–S3	2.300	2.120	0.370	0.615	2.144	0.144	2.149	0.370	0.665	2.342	-0.658
Fe3–N4	2.063	1.769	0.370	0.452			1.815	0.370	0.512		
Fe3–S1	2.387	2.120	0.370	0.486			2.149	0.370	0.526		
Fe3–S2	2.276	2.120	0.370	0.656			2.149	0.370	0.709		
Fe3–S4	2.282	2.120	0.370	0.645	2.239	0.239	2.149	0.370	0.698	2.445	-0.555
Fe4–S1	2.397	2.120	0.370	0.473			2.149	0.370	0.512		
Fe4–S3	2.281	2.120	0.370	0.647			2.149	0.370	0.700		
Fe4–S4	2.289	2.120	0.370	0.633			2.149	0.370	0.685		

Fe4–S8	2.286	2.120	0.370	0.638	2.392	0.392	2.149	0.370	0.691	2.587	-0.413
Fe5–N3	1.923	1.769	0.370	0.660			1.815	0.370	0.747		
Fe5–S5	2.270	2.120	0.370	0.667			2.149	0.370	0.721		
Fe5–S6	2.305	2.120	0.370	0.607			2.149	0.370	0.656		
Fe5–S7	2.297	2.120	0.370	0.620	2.553	0.553	2.149	0.370	0.670	2.794	-0.206
Fe6–N4	2.055	1.769	0.370	0.462			1.815	0.370	0.523		
Fe6–S1	2.425	2.120	0.370	0.439			2.149	0.370	0.474		
Fe6–S5	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe6–S6	2.295	2.120	0.370	0.623	2.160	0.160	2.149	0.370	0.674	2.360	-0.640
Fe7–N2	2.075	1.769	0.370	0.437			1.815	0.370	0.495		
Fe7–S1	2.391	2.120	0.370	0.481			2.149	0.370	0.520		
Fe7–S5	2.282	2.120	0.370	0.645			2.149	0.370	0.698		
Fe7–S7	2.278	2.120	0.370	0.652	2.216	0.216	2.149	0.370	0.706	2.419	-0.581
Fe8–S1	2.405	2.120	0.370	0.463			2.149	0.370	0.501		
Fe8–S6	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe8–S7	2.283	2.120	0.370	0.644			2.149	0.370	0.696		
Fe8–S9	2.276	2.120	0.370	0.656	2.403	0.403	2.149	0.370	0.709	2.599	-0.401
					18.676					20.358	

Table S107 The bond valence analyses of irons in P^N model compounds MUFQEK.

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–N1	1.922	1.769	0.370	0.661			1.815	0.370	0.749		
Fe1–S2	2.262	2.120	0.370	0.681			2.149	0.370	0.737		
Fe1–S3	2.296	2.120	0.370	0.621			2.149	0.370	0.672		
Fe1–S4	2.308	2.120	0.370	0.602	2.566	0.566	2.149	0.370	0.651	2.809	-0.191
Fe2–N2	2.072	1.769	0.370	0.441			1.815	0.370	0.499		
Fe2–S1	2.392	2.120	0.370	0.479			2.149	0.370	0.519		
Fe2–S2	2.270	2.120	0.370	0.667			2.149	0.370	0.721		
Fe2–S3	2.282	2.120	0.370	0.645	2.232	0.232	2.149	0.370	0.698	2.437	-0.563
Fe3–N4	2.088	1.769	0.370	0.422			1.815	0.370	0.478		
Fe3–S1	2.404	2.120	0.370	0.464			2.149	0.370	0.502		
Fe3–S2	2.282	2.120	0.370	0.645			2.149	0.370	0.698		
Fe3–S4	2.287	2.120	0.370	0.637	2.169	0.169	2.149	0.370	0.689	2.367	-0.633
Fe4–S1	2.411	2.120	0.370	0.455			2.149	0.370	0.493		
Fe4–S3	2.290	2.120	0.370	0.632			2.149	0.370	0.683		
Fe4–S4	2.278	2.120	0.370	0.652			2.149	0.370	0.706		

Fe4–S8	2.257	2.120	0.370	0.691	2.430	0.430	2.149	0.370	0.747	2.628	-0.372
Fe5–N3	1.895	1.769	0.370	0.711			1.815	0.370	0.806		
Fe5–S5	2.265	2.120	0.370	0.676			2.149	0.370	0.731		
Fe5–S6	2.293	2.120	0.370	0.627			2.149	0.370	0.678		
Fe5–S7	2.296	2.120	0.370	0.621	2.635	0.635	2.149	0.370	0.672	2.886	-0.114
Fe6–N4	2.057	1.769	0.370	0.459			1.815	0.370	0.520		
Fe6–S1	2.388	2.120	0.370	0.485			2.149	0.370	0.524		
Fe6–S5	2.255	2.120	0.370	0.694			2.149	0.370	0.751		
Fe6–S6	2.286	2.120	0.370	0.638	2.277	0.277	2.149	0.370	0.691	2.486	-0.514
Fe7–N2	2.072	1.769	0.370	0.441			1.815	0.370	0.499		
Fe7–S1	2.411	2.120	0.370	0.455			2.149	0.370	0.493		
Fe7–S5	2.291	2.120	0.370	0.630			2.149	0.370	0.681		
Fe7–S7	2.293	2.120	0.370	0.627	2.153	0.153	2.149	0.370	0.678	2.351	-0.649
Fe8–S1	2.398	2.120	0.370	0.472			2.149	0.370	0.510		
Fe8–S6	2.308	2.120	0.370	0.602			2.149	0.370	0.651		
Fe8–S7	2.274	2.120	0.370	0.660			2.149	0.370	0.713		
Fe8–S9	2.264	2.120	0.370	0.678	2.411	0.411	2.149	0.370	0.733	2.607	-0.393
					18.872					20.570	

Table S108 The bond valence analyses of irons in P^N model compounds MUFQIO.

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–N1	1.909	1.769	0.370	0.685			1.815	0.370	0.776		
Fe1–S2	2.271	2.120	0.370	0.665			2.149	0.370	0.719		
Fe1–S3	2.295	2.120	0.370	0.623			2.149	0.370	0.674		
Fe1–S4	2.296	2.120	0.370	0.621	2.594	0.594	2.149	0.370	0.672	2.841	-0.159
Fe2–N2	2.072	1.769	0.370	0.441			1.815	0.370	0.499		
Fe2–S1	2.395	2.120	0.370	0.476			2.149	0.370	0.514		
Fe2–S2	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe2–S3	2.272	2.120	0.370	0.663	2.241	0.241	2.149	0.370	0.717	2.446	-0.554
Fe3–N4	2.048	1.769	0.370	0.470			1.815	0.370	0.533		
Fe3–S1	2.437	2.120	0.370	0.425			2.149	0.370	0.459		
Fe3–S2	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe3–S4	2.291	2.120	0.370	0.630	2.162	0.162	2.149	0.370	0.681	2.362	-0.638
Fe4–S1	2.417	2.120	0.370	0.448			2.149	0.370	0.485		
Fe4–S3	2.290	2.120	0.370	0.632			2.149	0.370	0.683		
Fe4–S4	2.277	2.120	0.370	0.654			2.149	0.370	0.708		

Fe4–S5	2.292	2.120	0.370	0.628	2.362	0.362	2.149	0.370	0.679	2.555	-0.445
Fe1A–N1A	1.909	1.769	0.370	0.685			1.815	0.370	0.776		
Fe1A–S2A	2.271	2.120	0.370	0.665			2.149	0.370	0.719		
Fe1A–S3A	2.295	2.120	0.370	0.623			2.149	0.370	0.674		
Fe1A–S4A	2.296	2.120	0.370	0.621	2.594	0.594	2.149	0.370	0.672	2.841	-0.159
Fe2A–N2A	2.072	1.769	0.370	0.441			1.815	0.370	0.499		
Fe2A–S1	2.395	2.120	0.370	0.476			2.149	0.370	0.514		
Fe2A–S2A	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe2A–S3A	2.272	2.120	0.370	0.663	2.241	0.241	2.149	0.370	0.717	2.446	-0.554
Fe3A–N2	2.048	1.769	0.370	0.470			1.815	0.370	0.533		
Fe3–S1	2.437	2.120	0.370	0.425			2.149	0.370	0.459		
Fe3–S2A	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe3–S4A	2.291	2.120	0.370	0.630	2.162	0.162	2.149	0.370	0.681	2.362	-0.638
Fe4A–S1	2.417	2.120	0.370	0.448			2.149	0.370	0.485		
Fe4–S3A	2.290	2.120	0.370	0.632			2.149	0.370	0.683		
Fe4–S4A	2.277	2.120	0.370	0.654			2.149	0.370	0.708		
Fe4–S5A	2.292	2.120	0.370	0.628	2.362	0.362	2.149	0.370	0.679	2.555	-0.445
					18.719					20.407	

Table S109 The bond valence analyses of irons in P^N model compounds MUFQOU.

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–N1	1.901	1.769	0.370	0.700			1.815	0.370	0.793		
Fe1–S2	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe1–S3	2.280	2.120	0.370	0.649			2.149	0.370	0.702		
Fe1–S4	2.287	2.120	0.370	0.637	2.647	0.647	2.149	0.370	0.689	2.898	-0.102
Fe2–N2	2.044	1.769	0.370	0.476			1.815	0.370	0.539		
Fe2–S1	2.405	2.120	0.370	0.463			2.149	0.370	0.501		
Fe2–S2	2.279	2.120	0.370	0.651			2.149	0.370	0.704		
Fe2–S3	2.295	2.120	0.370	0.623	2.212	0.212	2.149	0.370	0.674	2.417	-0.583
Fe3–N3	2.050	1.769	0.370	0.468			1.815	0.370	0.530		
Fe3–S1	2.407	2.120	0.370	0.460			2.149	0.370	0.498		
Fe3–S2	2.277	2.120	0.370	0.654			2.149	0.370	0.708		
Fe3–S4	2.298	2.120	0.370	0.618	2.201	0.201	2.149	0.370	0.669	2.404	-0.596
Fe4–S1	2.385	2.120	0.370	0.489			2.149	0.370	0.528		
Fe4–S3	2.262	2.120	0.370	0.681			2.149	0.370	0.737		
Fe4–S4	2.273	2.120	0.370	0.661			2.149	0.370	0.715		

Fe4–S8	2.292	2.120	0.370	0.628	2.459	0.459	2.149	0.370	0.679	2.660	-0.340
Fe5–N4	1.927	1.769	0.370	0.652			1.815	0.370	0.739		
Fe5–S5	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe5–S6	2.302	2.120	0.370	0.611			2.149	0.370	0.661		
Fe5–S7	2.309	2.120	0.370	0.600	2.525	0.525	2.149	0.370	0.649	2.764	-0.236
Fe6–N3	2.075	1.769	0.370	0.437			1.815	0.370	0.495		
Fe6–S1	2.373	2.120	0.370	0.505			2.149	0.370	0.546		
Fe6–S5	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe6–S6	2.280	2.120	0.370	0.649	2.228	0.228	2.149	0.370	0.702	2.432	-0.568
Fe7–N2	2.076	1.769	0.370	0.436			1.815	0.370	0.494		
Fe7–S1	2.394	2.120	0.370	0.477			2.149	0.370	0.516		
Fe7–S5	2.288	2.120	0.370	0.635			2.149	0.370	0.687		
Fe7–S7	2.287	2.120	0.370	0.637	2.185	0.185	2.149	0.370	0.689	2.385	-0.615
Fe8–S1	2.403	2.120	0.370	0.465			2.149	0.370	0.503		
Fe8–S6	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe8–S7	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe8–S9	2.306	2.120	0.370	0.605	2.347	0.347	2.149	0.370	0.654	2.539	-0.461
					18.804					20.499	

Table S110 The bond valence analyses of irons in P^N model compounds MUFQUA.

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–S2	2.238	2.120	0.370	0.727			2.149	0.370	0.786		
Fe1–S3	2.272	2.120	0.370	0.663			2.149	0.370	0.717		
Fe1–S4	2.271	2.120	0.370	0.665			2.149	0.370	0.719		
Fe1–S10	2.229	2.120	0.370	0.745	2.800	0.800	2.149	0.370	0.806	3.028	0.028
Fe2–N1	2.060	1.769	0.370	0.455			1.815	0.370	0.516		
Fe2–S1	2.398	2.120	0.370	0.472			2.149	0.370	0.510		
Fe2–S2	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe2–S3	2.292	2.120	0.370	0.628	2.196	0.196	2.149	0.370	0.679	2.398	-0.602
Fe3–N2	2.048	1.769	0.370	0.470			1.815	0.370	0.533		
Fe3–S1	2.415	2.120	0.370	0.451			2.149	0.370	0.487		
Fe3–S2	2.294	2.120	0.370	0.625			2.149	0.370	0.676		
Fe3–S4	2.283	2.120	0.370	0.644	2.190	0.190	2.149	0.370	0.696	2.392	-0.608
Fe4–S1	2.351	2.120	0.370	0.536			2.149	0.370	0.579		
Fe4–S3	2.272	2.120	0.370	0.663			2.149	0.370	0.717		
Fe4–S4	2.262	2.120	0.370	0.681			2.149	0.370	0.737		

Fe4–S8	2.334	2.120	0.370	0.561	2.441	0.441	2.149	0.370	0.607	2.640	-0.360
Fe5–S5	2.245	2.120	0.370	0.713			2.149	0.370	0.771		
Fe5–S6	2.272	2.120	0.370	0.663			2.149	0.370	0.717		
Fe5–S7	2.281	2.120	0.370	0.647			2.149	0.370	0.700		
Fe5–S11	2.245	2.120	0.370	0.713	2.737	0.737	2.149	0.370	0.771	2.960	-0.040
Fe6–N2	2.044	1.769	0.370	0.476			1.815	0.370	0.539		
Fe6–S1	2.368	2.120	0.370	0.512			2.149	0.370	0.553		
Fe6–S5	2.283	2.120	0.370	0.644			2.149	0.370	0.696		
Fe6–S6	2.280	2.120	0.370	0.649	2.280	0.280	2.149	0.370	0.702	2.490	-0.510
Fe7–N1	2.044	1.769	0.370	0.476			1.815	0.370	0.539		
Fe7–S1	2.384	2.120	0.370	0.490			2.149	0.370	0.530		
Fe7–S5	2.292	2.120	0.370	0.628			2.149	0.370	0.679		
Fe7–S7	2.284	2.120	0.370	0.642	2.236	0.236	2.149	0.370	0.694	2.442	-0.558
Fe8–S1	2.397	2.120	0.370	0.473			2.149	0.370	0.512		
Fe8–S6	2.258	2.120	0.370	0.689			2.149	0.370	0.745		
Fe8–S7	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe8–S9	2.307	2.120	0.370	0.603	2.426	0.426	2.149	0.370	0.652	2.624	-0.376
					19.304					20.974	

Table S111 The bond valence analyses of irons in P^N model compounds MUFRAH.

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–S10	2.252	2.120	0.370	0.700			2.149	0.370	0.757		
Fe1–S2	2.223	2.120	0.370	0.757			2.149	0.370	0.819		
Fe1–S3	2.281	2.120	0.370	0.647			2.149	0.370	0.700		
Fe1–S4	2.277	2.120	0.370	0.654	2.758	0.758	2.149	0.370	0.708	2.983	-0.017
Fe2–N1	2.059	1.769	0.370	0.457			1.815	0.370	0.517		
Fe2–S1	2.406	2.120	0.370	0.462			2.149	0.370	0.499		
Fe2–S2	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe2–S3	2.281	2.120	0.370	0.647	2.206	0.206	2.149	0.370	0.700	2.409	-0.591
Fe3–N2	2.062	1.769	0.370	0.453			1.815	0.370	0.513		
Fe3–S1	2.411	2.120	0.370	0.455			2.149	0.370	0.493		
Fe3–S2	2.283	2.120	0.370	0.644			2.149	0.370	0.696		
Fe3–S4	2.282	2.120	0.370	0.645	2.198	0.198	2.149	0.370	0.698	2.400	-0.600
Fe4–S1	2.430	2.120	0.370	0.433			2.149	0.370	0.468		
Fe4–S3	2.299	2.120	0.370	0.616			2.149	0.370	0.667		
Fe4–S4	2.295	2.120	0.370	0.623			2.149	0.370	0.674		

Fe4–S8	2.312	2.120	0.370	0.595	2.267	0.267	2.149	0.370	0.644	2.452	-0.548
Fe5–S11	2.254	2.120	0.370	0.696			2.149	0.370	0.753		
Fe5–S5	2.258	2.120	0.370	0.689			2.149	0.370	0.745		
Fe5–S6	2.275	2.120	0.370	0.658			2.149	0.370	0.711		
Fe5–S7	2.269	2.120	0.370	0.669	2.711	0.711	2.149	0.370	0.723	2.932	-0.068
Fe6–N2	2.054	1.769	0.370	0.463			1.815	0.370	0.524		
Fe6–S1	2.398	2.120	0.370	0.472			2.149	0.370	0.510		
Fe6–S5	2.295	2.120	0.370	0.623			2.149	0.370	0.674		
Fe6–S6	2.269	2.120	0.370	0.669	2.226	0.226	2.149	0.370	0.723	2.431	-0.569
Fe7–N1	2.047	1.769	0.370	0.472			1.815	0.370	0.534		
Fe7–S1	2.405	2.120	0.370	0.463			2.149	0.370	0.501		
Fe7–S5	2.286	2.120	0.370	0.638			2.149	0.370	0.691		
Fe7–S7	2.272	2.120	0.370	0.663	2.236	0.236	2.149	0.370	0.717	2.443	-0.557
Fe8–S1	2.384	2.120	0.370	0.490			2.149	0.370	0.530		
Fe8–S6	2.274	2.120	0.370	0.660			2.149	0.370	0.713		
Fe8–S7	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe8–S9	2.325	2.120	0.370	0.575	2.361	0.361	2.149	0.370	0.621	2.553	-0.447
					18.963					20.603	

Table S112 The bond valence analyses of irons in P^N model compounds MUFREL.

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	2.248	2.120	0.370	0.708			2.149	0.370	0.765		
Fe1–S2	2.276	2.120	0.370	0.656			2.149	0.370	0.709		
Fe1–S3	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe1–S8	2.227	2.120	0.370	0.749	2.774	0.774	2.149	0.370	0.810	3.000	0.000
Fe2–N1	2.048	1.769	0.370	0.470			1.815	0.370	0.533		
Fe2–S1	2.271	2.120	0.370	0.665			2.149	0.370	0.719		
Fe2–S2	2.288	2.120	0.370	0.635			2.149	0.370	0.687		
Fe2–S4	2.378	2.120	0.370	0.498	2.268	0.268	2.149	0.370	0.539	2.477	-0.523
Fe3–N2	2.044	1.769	0.370	0.476			1.815	0.370	0.539		
Fe3–S1	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe3–S3	2.295	2.120	0.370	0.623			2.149	0.370	0.674		
Fe3–S4	2.418	2.120	0.370	0.447	2.188	0.188	2.149	0.370	0.483	2.390	-0.610
Fe4–S2	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe4–S3	2.276	2.120	0.370	0.656			2.149	0.370	0.709		
Fe4–S4	2.406	2.120	0.370	0.462			2.149	0.370	0.499		

Fe4–S10	2.321	2.120	0.370	0.581	2.335	0.335	2.149	0.370	0.628	2.526	-0.474
Fe5–N1	2.068	1.769	0.370	0.446			1.815	0.370	0.505		
Fe5–S5	2.279	2.120	0.370	0.651			2.149	0.370	0.704		
Fe5–S6	2.304	2.120	0.370	0.608			2.149	0.370	0.658		
Fe5–S4	2.406	2.120	0.370	0.462	2.166	0.166	2.149	0.370	0.499	2.365	-0.635
Fe6–N2	2.034	1.769	0.370	0.489			1.815	0.370	0.553		
Fe6–S4	2.386	2.120	0.370	0.487			2.149	0.370	0.527		
Fe6–S5	2.268	2.120	0.370	0.670			2.149	0.370	0.725		
Fe6–S7	2.283	2.120	0.370	0.644	2.290	0.290	2.149	0.370	0.696	2.501	-0.499
Fe7–S6	2.283	2.120	0.370	0.644			2.149	0.370	0.696		
Fe7–S11	2.314	2.120	0.370	0.592			2.149	0.370	0.640		
Fe7–S4	2.406	2.120	0.370	0.462			2.149	0.370	0.499		
Fe7–S7	2.278	2.120	0.370	0.652	2.350	0.350	2.149	0.370	0.706	2.541	-0.459
Fe8–S5	2.243	2.120	0.370	0.717			2.149	0.370	0.776		
Fe8–S6	2.280	2.120	0.370	0.649			2.149	0.370	0.702		
Fe8–S7	2.271	2.120	0.370	0.665			2.149	0.370	0.719		
Fe8–S9	2.228	2.120	0.370	0.747	2.778	0.778	2.149	0.370	0.808	3.004	0.004
					19.149					20.805	

Table S113 The bond valence analyses of irons in P^N model compounds NIFWOQ.

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–N1	1.913	1.769	0.370	0.678			1.815	0.370	0.767		
Fe1–S2	2.268	2.120	0.370	0.670			2.149	0.370	0.725		
Fe1–S3	2.277	2.120	0.370	0.654			2.149	0.370	0.708		
Fe1–S4	2.278	2.120	0.370	0.652	2.655	0.655	2.149	0.370	0.706	2.905	-0.095
Fe2–N2	2.002	1.769	0.370	0.533			1.815	0.370	0.603		
Fe2–S1	2.398	2.120	0.370	0.472			2.149	0.370	0.510		
Fe2–S2	2.258	2.120	0.370	0.689			2.149	0.370	0.745		
Fe2–S3	2.288	2.120	0.370	0.635	2.328	0.328	2.149	0.370	0.687	2.545	-0.455
Fe3–N2A	2.071	1.769	0.370	0.442			1.815	0.370	0.501		
Fe3–S1	2.396	2.120	0.370	0.474			2.149	0.370	0.513		
Fe3–S2	2.249	2.120	0.370	0.706			2.149	0.370	0.763		
Fe3–S4	2.282	2.120	0.370	0.645	2.267	0.267	2.149	0.370	0.698	2.475	-0.525
Fe4–S1	2.363	2.120	0.370	0.519			2.149	0.370	0.561		
Fe4–S3	2.246	2.120	0.370	0.711			2.149	0.370	0.769		
Fe4–S4	2.270	2.120	0.370	0.667			2.149	0.370	0.721		

Fe4–S5/6	2.439	2.120	0.370	0.422	2.319	0.319	2.149	0.370	0.457	2.508	-0.492
Fe1A–N1A	1.938	1.769	0.370	0.633			1.815	0.370	0.717		
Fe1A–S2A	2.268	2.120	0.370	0.670			2.149	0.370	0.725		
Fe1A–S3A	2.277	2.120	0.370	0.654			2.149	0.370	0.708		
Fe1A–S4A	2.278	2.120	0.370	0.652	2.610	0.610	2.149	0.370	0.706	2.855	-0.145
Fe2A–N2A	2.164	1.769	0.370	0.344			1.815	0.370	0.389		
Fe2A–S1	2.398	2.120	0.370	0.472			2.149	0.370	0.510		
Fe2A–S2A	2.258	2.120	0.370	0.689			2.149	0.370	0.745		
Fe2A–S3A	2.288	2.120	0.370	0.635	2.139	0.139	2.149	0.370	0.687	2.331	-0.669
Fe3A–N2	2.062	1.769	0.370	0.453			1.815	0.370	0.513		
Fe3A–S1	2.396	2.120	0.370	0.474			2.149	0.370	0.513		
Fe3A–S2A	2.249	2.120	0.370	0.706			2.149	0.370	0.763		
Fe3A–S4A	2.282	2.120	0.370	0.645	2.278	0.278	2.149	0.370	0.698	2.487	-0.513
Fe4A–S1	2.363	2.120	0.370	0.519			2.149	0.370	0.561		
Fe4A–S3A	2.246	2.120	0.370	0.711			2.149	0.370	0.769		
Fe4A–S4A	2.270	2.120	0.370	0.667			2.149	0.370	0.721		
Fe4A–S5A	2.413	2.120	0.370	0.453	2.350	0.350	2.149	0.370	0.490	2.541	-0.459
					18.947					20.648	

Table S114 The bond valence analyses of irons in P^N model compounds NIFWUW.

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–N1	1.919	1.769	0.370	0.667			1.815	0.370	0.755		
Fe1–S2	2.274	2.120	0.370	0.660			2.149	0.370	0.713		
Fe1–S3	2.296	2.120	0.370	0.621			2.149	0.370	0.672		
Fe1–S4	2.300	2.120	0.370	0.615	2.562	0.562	2.149	0.370	0.665	2.805	-0.195
Fe2–N2	2.071	1.769	0.370	0.442			1.815	0.370	0.501		
Fe2–S1	2.404	2.120	0.370	0.464			2.149	0.370	0.502		
Fe2–S2	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe2–S3	2.283	2.120	0.370	0.644	2.192	0.192	2.149	0.370	0.696	2.393	-0.607
Fe3–N4	2.130	1.769	0.370	0.377			1.815	0.370	0.427		
Fe3–S1	2.410	2.120	0.370	0.457			2.149	0.370	0.494		
Fe3–S2	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe3–S4	2.290	2.120	0.370	0.632	2.118	0.118	2.149	0.370	0.683	2.310	-0.690
Fe4–S1	2.360	2.120	0.370	0.523			2.149	0.370	0.565		
Fe4–S3	2.276	2.120	0.370	0.656			2.149	0.370	0.709		
Fe4–S4	2.269	2.120	0.370	0.669			2.149	0.370	0.723		

Fe4–S8	2.344	2.120	0.370	0.546	2.393	0.393	2.149	0.370	0.590	2.588	-0.412
Fe5–N3	1.926	1.769	0.370	0.654			1.815	0.370	0.741		
Fe5–S5	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe5–S6	2.295	2.120	0.370	0.623			2.149	0.370	0.674		
Fe5–S7	2.309	2.120	0.370	0.600	2.514	0.514	2.149	0.370	0.649	2.752	-0.248
Fe6–N4	2.008	1.769	0.370	0.524			1.815	0.370	0.594		
Fe6–S1	2.388	2.120	0.370	0.485			2.149	0.370	0.524		
Fe6–S5	2.276	2.120	0.370	0.656			2.149	0.370	0.709		
Fe6–S6	2.295	2.120	0.370	0.623	2.288	0.288	2.149	0.370	0.674	2.501	-0.499
Fe7–N2	2.046	1.769	0.370	0.473			1.815	0.370	0.536		
Fe7–S1	2.390	2.120	0.370	0.482			2.149	0.370	0.521		
Fe7–S5	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe7–S7	2.295	2.120	0.370	0.623	2.220	0.220	2.149	0.370	0.674	2.425	-0.575
Fe8–S1	2.355	2.120	0.370	0.530			2.149	0.370	0.573		
Fe8–S6	2.280	2.120	0.370	0.649			2.149	0.370	0.702		
Fe8–S7	2.251	2.120	0.370	0.702			2.149	0.370	0.759		
Fe8–S9	2.338	2.120	0.370	0.555	2.435	0.435	2.149	0.370	0.600	2.634	-0.366
					18.723					20.409	

Table S115 The bond valence analyses of irons in P^N model compounds NIFXAD.

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–N1	1.915	1.769	0.370	0.674			1.815	0.370	0.763		
Fe1–S2	2.275	2.120	0.370	0.658			2.149	0.370	0.711		
Fe1–S3	2.304	2.120	0.370	0.608			2.149	0.370	0.658		
Fe1–S4	2.277	2.120	0.370	0.654	2.594	0.594	2.149	0.370	0.708	2.840	-0.160
Fe2–N2	2.058	1.769	0.370	0.458			1.815	0.370	0.519		
Fe2–S1	2.387	2.120	0.370	0.486			2.149	0.370	0.526		
Fe2–S2	2.276	2.120	0.370	0.656			2.149	0.370	0.709		
Fe2–S3	2.291	2.120	0.370	0.630	2.230	0.230	2.149	0.370	0.681	2.435	-0.565
Fe3–N2A	2.055	1.769	0.370	0.462			1.815	0.370	0.523		
Fe3–S1	2.401	2.120	0.370	0.468			2.149	0.370	0.506		
Fe3–S2	2.289	2.120	0.370	0.633			2.149	0.370	0.685		
Fe3–S4	2.289	2.120	0.370	0.633	2.196	0.196	2.149	0.370	0.685	2.399	-0.601
Fe4–S1	2.351	2.120	0.370	0.536			2.149	0.370	0.579		
Fe4–S3	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe4–S4	2.258	2.120	0.370	0.689			2.149	0.370	0.745		

Fe4–S5	2.344	2.120	0.370	0.546	2.423	0.423	2.149	0.370	0.590	2.620	-0.380
Fe1A–N1A	1.915	1.769	0.370	0.674			1.815	0.370	0.763		
Fe1A–S2A	2.275	2.120	0.370	0.658			2.149	0.370	0.711		
Fe1A–S3A	2.304	2.120	0.370	0.608			2.149	0.370	0.658		
Fe1A–S4A	2.277	2.120	0.370	0.654	2.594	0.594	2.149	0.370	0.708	2.840	-0.160
Fe2A–N2A	2.058	1.769	0.370	0.458			1.815	0.370	0.519		
Fe2A–S1	2.387	2.120	0.370	0.486			2.149	0.370	0.526		
Fe2A–S2A	2.276	2.120	0.370	0.656			2.149	0.370	0.709		
Fe2A–S3A	2.291	2.120	0.370	0.630	2.230	0.230	2.149	0.370	0.681	2.435	-0.565
Fe3A–N2	2.055	1.769	0.370	0.462			1.815	0.370	0.523		
Fe3A–S1	2.401	2.120	0.370	0.468			2.149	0.370	0.506		
Fe3A–S2A	2.289	2.120	0.370	0.633			2.149	0.370	0.685		
Fe3A–S4A	2.289	2.120	0.370	0.633	2.196	0.196	2.149	0.370	0.685	2.399	-0.601
Fe4A–S1	2.351	2.120	0.370	0.536			2.149	0.370	0.579		
Fe4A–S3A	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe4A–S4A	2.258	2.120	0.370	0.689			2.149	0.370	0.745		
Fe4A–S5A	2.344	2.120	0.370	0.546	2.423	0.423	2.149	0.370	0.590	2.620	-0.380
					18.885					20.587	

Table S116 The bond valence analyses of irons in P^N model compounds WUZDAW.

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–N1	1.919	1.769	0.370	0.667			1.815	0.370	0.755		
Fe1–S2	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe1–S3	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe1–S4	2.289	2.120	0.370	0.633	2.584	0.584	2.149	0.370	0.685	2.829	-0.171
Fe2–N2	2.058	1.769	0.370	0.458			1.815	0.370	0.519		
Fe2–S1	2.372	2.120	0.370	0.506			2.149	0.370	0.547		
Fe2–S2	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe2–S3	2.286	2.120	0.370	0.638	2.239	0.239	2.149	0.370	0.691	2.445	-0.555
Fe3–N2C	2.060	1.769	0.370	0.455			1.815	0.370	0.516		
Fe3–S1	2.397	2.120	0.370	0.473			2.149	0.370	0.512		
Fe3–S2	2.296	2.120	0.370	0.621			2.149	0.370	0.672		
Fe3–S4	2.305	2.120	0.370	0.607	2.156	0.156	2.149	0.370	0.656	2.355	-0.645
Fe4–S1	2.349	2.120	0.370	0.539			2.149	0.370	0.582		
Fe4–S3	2.277	2.120	0.370	0.654			2.149	0.370	0.708		
Fe4–S4	2.256	2.120	0.370	0.692			2.149	0.370	0.749		

Fe4–S5	2.315	2.120	0.370	0.590	2.476	0.476	2.149	0.370	0.638	2.677	-0.323
Fe1C–N1C	1.919	1.769	0.370	0.667			1.815	0.370	0.755		
Fe1C–S2C	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe1C–S3C	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe1C–S4C	2.289	2.120	0.370	0.633	2.584	0.584	2.149	0.370	0.685	2.829	-0.171
Fe2C–N2C	2.058	1.769	0.370	0.458			1.815	0.370	0.519		
Fe2C–S1	2.372	2.120	0.370	0.506			2.149	0.370	0.547		
Fe2C–S2C	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe2C–S3C	2.286	2.120	0.370	0.638	2.239	0.239	2.149	0.370	0.691	2.445	-0.555
Fe3C–N2	2.060	1.769	0.370	0.455			1.815	0.370	0.516		
Fe3C–S1	2.397	2.120	0.370	0.473			2.149	0.370	0.512		
Fe3C–S2C	2.296	2.120	0.370	0.621			2.149	0.370	0.672		
Fe3C–S4C	2.305	2.120	0.370	0.607	2.156	0.156	2.149	0.370	0.656	2.355	-0.645
Fe4A–S1	2.349	2.120	0.370	0.539			2.149	0.370	0.582		
Fe4A–S3C	2.277	2.120	0.370	0.654			2.149	0.370	0.708		
Fe4A–S4C	2.256	2.120	0.370	0.692			2.149	0.370	0.749		
Fe4A–S5C	2.315	2.120	0.370	0.590	2.476	0.476	2.149	0.370	0.638	2.677	-0.323
					18.910					20.613	

References

1 F. A. Tezcan, J. T. Kaiser, J. B. Howard and D. C. Rees, *J. Am. Chem. Soc.*, 2015, **137**, 146−149.
2 J. Kim, D. Woo and D. C. Rees, *Biochemistry*, 1993, **32**, 7104−7115.
3 H. Schindelin, C. Kisker, J. L. Schlessman, J. B. Howard and D. C. Rees, *Nature*, 1997, **387**, 370−376.
4 R. Sarma, B. M. Barney, S. Keable, D. R. Dean, L. C. Seefeldt and J. W. Peters, *J. Inorg. Biochem.*, 2010, **104**, 385−389.
5 H. L. Rutledge, J. Rittle, L. M. Williamson, W. A. Xu, D. M. Gagnon and F. A. Tezcan, *J. Am. Chem. Soc.*, 2019, **141**, 10091−10098.
6 B. Schmid, O. Einsle, H. J. Chiu, A. Willing, M. Yoshida, J. B. Howard and D. C. Rees, *Biochemistry*, 2002, **41**, 15557−15565.
7 F. Tezcan, J. Kaiser, D. Mustafi, M. Walton, J. Howard and D. Rees, *Science*, 2005, **309**, 1377−1380.
8 S. M. Keable, J. Vertemara, O. A. Zadvornyy, B. J. Eilers, K. Danyal, A. J. Rasmussen, L. De Gioia, G. Zampella, L. C. Seefeldt and J. W. Peters, *J. Inorg. Biochem.*, 2018, **180**, 129−134.
9 J. T. Henthorn, R. J. Arias, S. Koroidov, T. Kroll, D. Sokaras, U. Bergmann, D. C. Rees and S. DeBeer, *J. Am. Chem. Soc.*, 2019, **141**, 13676−13688.