Supporting information

Comparisons of bond valences and distances for CO- and N_2-bound clusters of FeMo-cofactors

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Figure and Table Options

Table S1 The bond valence analyses for irons in FeMo-cofactor (1) from MoFe protein 3U7Q which perform the most accurate structure with resolution of 1.00 Å.

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	2.306	2.120	0.370	0.605			2.149	0.370	0.654		
Fe1–S2A	2.270	2.120	0.370	0.667			2.149	0.370	0.721		
Fe1–S4A	2.289	2.120	0.370	0.633			2.149	0.370	0.685		
Fe1–SG	2.265	2.120	0.370	0.676	2.581	0.581	2.149	0.370	0.731	**2.791**	-0.209
Fe2–S1A	2.263	2.120	0.370	0.679			2.149	0.370	0.735		
Fe2–S2A	2.246	2.120	0.370	0.711			2.149	0.370	0.769		
Fe2–S2B	2.198	2.120	0.370	0.810			2.149	0.370	0.876		
Fe2–CX	2.014	1.650	0.370	0.374	2.575	0.575	1.689	0.370	0.415	**2.796**	-0.204
Fe3–S2A	2.267	2.120	0.370	0.672			2.149	0.370	0.727		
Fe3–S4A	2.251	2.120	0.370	0.702			2.149	0.370	0.759		
Fe3–S5A	2.229	2.120	0.370	0.745			2.149	0.370	0.806		
Fe3–CX	1.990	1.650	0.370	0.399	2.518	0.518	1.689	0.370	0.443	**2.735**	-0.265
Fe4–S1A	2.286	2.120	0.370	0.638			2.149	0.370	0.691		
Fe4–S3A	2.240	2.120	0.370	0.723			2.149	0.370	0.782		
Fe4–S4A	2.286	2.120	0.370	0.638			2.149	0.370	0.691		
Fe4–CX	2.003	1.650	0.370	0.385	**2.385**	0.385	1.689	0.370	0.428	2.591	-0.409

Fe5–S1B	2.261	2.120	0.370	0.683			2.149	0.370	0.739		
Fe5–S3A	2.261	2.120	0.370	0.683			2.149	0.370	0.739		
Fe5–S4B	2.256	2.120	0.370	0.692			2.149	0.370	0.749		
Fe5–CX	2.006	1.650	0.370	0.382	2.441	0.441	1.689	0.370	0.425	**2.651**	-0.349
Fe6–S1B	2.237	2.120	0.370	0.729			2.149	0.370	0.788		
Fe6–S3B	2.220	2.120	0.370	0.763			2.149	0.370	0.825		
Fe6–S2B	2.178	2.120	0.370	0.855			2.149	0.370	0.925		
Fe6–CX	2.008	1.650	0.370	0.380	2.727	0.727	1.689	0.370	0.422	**2.961**	-0.039
Fe7–S3B	2.253	2.120	0.370	0.698			2.149	0.370	0.755		
Fe7–S4B	2.221	2.120	0.370	0.761			2.149	0.370	0.823		
Fe7–S5A	2.213	2.120	0.370	0.778			2.149	0.370	0.841		
Fe7–CX	1.979	1.650	0.370	0.411	2.648	0.648	1.689	0.370	0.457	**2.876**	-0.124

Table S2 The bond valence analyses for irons in FeMo-cofactor (2) from MoFe protein 3U7Q which perform the most accurate structure with resolution of 1.00 Å.

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	2.295	2.120	0.370	0.623			2.149	0.370	0.674		
Fe1–S2A	2.266	2.120	0.370	0.674			2.149	0.370	0.729		
Fe1–S4A	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe1–SG	2.269	2.120	0.370	0.669	2.602	0.602	2.149	0.370	0.723	**2.815**	-0.185
Fe2–S1A	2.261	2.120	0.370	0.683			2.149	0.370	0.739		
Fe2–S2A	2.254	2.120	0.370	0.696			2.149	0.370	0.753		
Fe2–S2B	2.206	2.120	0.370	0.793			2.149	0.370	0.857		
Fe2–CX	1.997	1.650	0.370	0.391	2.563	0.563	1.689	0.370	0.435	**2.784**	-0.216
Fe3–S2A	2.275	2.120	0.370	0.658			2.149	0.370	0.711		
Fe3–S4A	2.254	2.120	0.370	0.696			2.149	0.370	0.753		
Fe3–S5A	2.221	2.120	0.370	0.761			2.149	0.370	0.823		
Fe3–CX	1.984	1.650	0.370	0.405	2.521	0.521	1.689	0.370	0.451	**2.738**	-0.262
Fe4–S1A	2.286	2.120	0.370	0.638			2.149	0.370	0.691		
Fe4–S3A	2.240	2.120	0.370	0.723			2.149	0.370	0.782		
Fe4–S4A	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe4–CX	1.991	1.650	0.370	0.398	**2.396**	0.396	1.689	0.370	0.442	2.603	-0.397

Fe5–S1B	2.268	2.120	0.370	0.670			2.149	0.370	0.725		
Fe5–S3A	2.261	2.120	0.370	0.683			2.149	0.370	0.739		
Fe5–S4B	2.250	2.120	0.370	0.704			2.149	0.370	0.761		
Fe5–CX	2.008	1.650	0.370	0.380	2.437	0.437	1.689	0.370	0.422	**2.647**	-0.353
Fe6–S1B	2.234	2.120	0.370	0.735			2.149	0.370	0.795		
Fe6–S3B	2.219	2.120	0.370	0.765			2.149	0.370	0.828		
Fe6–S2B	2.173	2.120	0.370	0.867			2.149	0.370	0.937		
Fe6–CX	2.018	1.650	0.370	0.370	2.736	0.736	1.689	0.370	0.411	**2.971**	-0.029
Fe7–S3B	2.246	2.120	0.370	0.711			2.149	0.370	0.769		
Fe7–S4B	2.220	2.120	0.370	0.763			2.149	0.370	0.825		
Fe7–S5A	2.210	2.120	0.370	0.784			2.149	0.370	0.848		
Fe7–CX	1.997	1.650	0.370	0.391	2.650	0.650	1.689	0.370	0.435	**2.878**	-0.122

Table S3 The bond valence analyses for irons in FeMo-cofactor (1) from MoFe protein 4TKV which coordinated with single CO between Fe2 and Fe6 with resolution of 1.50 Å.

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	2.281	2.120	0.370	0.647			2.149	0.370	0.700		
Fe1–S2A	2.250	2.120	0.370	0.704			2.149	0.370	0.761		
Fe1–S4A	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe1–SG	2.264	2.120	0.370	0.678	2.665	0.665	2.149	0.370	0.733	**2.883**	-0.117
Fe2–S1A	2.224	2.120	0.370	0.755			2.149	0.370	0.817		
Fe2–S2A	2.217	2.120	0.370	0.769			2.149	0.370	0.832		
Fe2–S2B	1.856	1.470	0.370	0.352			1.689	0.370	0.637		
Fe2–CX	2.004	1.650	0.370	0.384	2.482	0.482	1.689	0.370	0.427	**2.712**	-0.288
Fe3–S2A	2.294	2.120	0.370	0.625			2.149	0.370	0.676		
Fe3–S4A	2.258	2.120	0.370	0.689			2.149	0.370	0.745		
Fe3–S5A	2.197	2.120	0.370	0.812			2.149	0.370	0.878		
Fe3–CX	1.962	1.650	0.370	0.430	2.556	0.556	1.689	0.370	0.478	**2.777**	-0.223
Fe4–S1A	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe4–S3A	2.244	2.120	0.370	0.715			2.149	0.370	0.774		
Fe4–S4A	2.310	2.120	0.370	0.598			2.149	0.370	0.647		
Fe4–CX	1.986	1.650	0.370	0.403	**2.357**	0.357	1.689	0.370	0.448	2.561	-0.439

Fe5–S1B	2.272	2.120	0.370	0.663			2.149	0.370	0.717		
Fe5–S3A	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe5–S4B	2.204	2.120	0.370	0.797			2.149	0.370	0.862		
Fe5–CX	2.009	1.650	0.370	0.379	2.500	0.500	1.689	0.370	0.421	**2.715**	-0.285
Fe6–S1B	2.166	2.120	0.370	0.883			2.149	0.370	0.955		
Fe6–S3B	2.189	2.120	0.370	0.830			2.149	0.370	0.898		
Fe6–S2B	1.852	1.470	0.370	0.356			1.689	0.370	0.644		
Fe6–CX	2.008	1.650	0.370	0.380	2.672	0.672	1.689	0.370	0.422	**2.919**	-0.081
Fe7–S3B	2.218	2.120	0.370	0.767			2.149	0.370	0.830		
Fe7–S4B	2.225	2.120	0.370	0.753			2.149	0.370	0.814		
Fe7–S5A	2.212	2.120	0.370	0.780			2.149	0.370	0.843		
Fe7–CX	1.961	1.650	0.370	0.431	2.732	0.732	1.689	0.370	0.479	**2.967**	-0.033

Table S4 The bond valence analyses for irons in FeMo-cofactor (2) from MoFe protein 4TKV which coordinated with single CO between Fe2 and Fe6 with resolution of 1.50 Å.

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	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe1–S2A	2.234	2.120	0.370	0.735			2.149	0.370	0.795		
Fe1–S4A	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe1–SG	2.250	2.120	0.370	0.704	2.719	0.719	2.149	0.370	0.761	**2.941**	-0.059
Fe2–S1A	2.219	2.120	0.370	0.765			2.149	0.370	0.828		
Fe2–S2A	2.229	2.120	0.370	0.745			2.149	0.370	0.806		
Fe2–S2B	1.865	1.470	0.370	0.344			1.689	0.370	0.621		
Fe2–CX	1.998	1.650	0.370	0.390	2.460	0.460	1.689	0.370	0.434	**2.688**	-0.312
Fe3–S2A	2.281	2.120	0.370	0.647			2.149	0.370	0.700		
Fe3–S4A	2.253	2.120	0.370	0.698			2.149	0.370	0.755		
Fe3–S5A	2.199	2.120	0.370	0.808			2.149	0.370	0.874		
Fe3–CX	1.970	1.650	0.370	0.421	2.574	0.574	1.689	0.370	0.468	**2.796**	-0.204
Fe4–S1A	2.292	2.120	0.370	0.628			2.149	0.370	0.679		
Fe4–S3A	2.244	2.120	0.370	0.715			2.149	0.370	0.774		
Fe4–S4A	2.280	2.120	0.370	0.649			2.149	0.370	0.702		
Fe4–CX	1.995	1.650	0.370	0.394	**2.386**	0.386	1.689	0.370	0.437	2.592	-0.408

Fe5–S1B	2.281	2.120	0.370	0.647			2.149	0.370	0.700		
Fe5–S3A	2.269	2.120	0.370	0.669			2.149	0.370	0.723		
Fe5–S4B	2.212	2.120	0.370	0.780			2.149	0.370	0.843		
Fe5–CX	2.010	1.650	0.370	0.378	2.473	0.473	1.689	0.370	0.420	**2.686**	-0.314
Fe6–S1B	2.181	2.120	0.370	0.848			2.149	0.370	0.917		
Fe6–S3B	2.196	2.120	0.370	0.814			2.149	0.370	0.881		
Fe6–S2B	1.865	1.470	0.370	0.344			1.689	0.370	0.621		
Fe6–CX	2.017	1.650	0.370	0.371	2.592	0.592	1.689	0.370	0.412	**2.831**	-0.169
Fe7–S3B	2.232	2.120	0.370	0.739			2.149	0.370	0.799		
Fe7–S4B	2.233	2.120	0.370	0.737			2.149	0.370	0.797		
Fe7–S5A	2.192	2.120	0.370	0.823			2.149	0.370	0.890		
Fe7–CX	1.978	1.650	0.370	0.412	2.711	0.711	1.689	0.370	0.458	**2.944**	-0.056

Table S5 The bond valence analyses for irons in FeMo-cofactor (1) from MoFe protein 7JRF which coordinated with double CO on Fe6 with resolution of 1.33 Å.

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	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe1–S2A	2.258	2.120	0.370	0.689			2.149	0.370	0.745		
Fe1–S4A	2.299	2.120	0.370	0.616			2.149	0.370	0.667		
Fe1–SG	2.283	2.120	0.370	0.644	2.589	0.589	2.149	0.370	0.696	**2.800**	-0.200
Fe2–S1A	2.218	2.120	0.370	0.767			2.149	0.370	0.830		
Fe2–S2A	2.233	2.120	0.370	0.737			2.149	0.370	0.797		
Fe2–C1	1.928	1.650	0.370	0.472			1.689	0.370	0.524		
Fe2–CX	1.967	1.650	0.370	0.425	2.400	0.400	1.689	0.370	0.472	**2.623**	-0.377
Fe3–S2A	2.275	2.120	0.370	0.658			2.149	0.370	0.711		
Fe3–S4A	2.251	2.120	0.370	0.702			2.149	0.370	0.759		
Fe3–S5A	2.233	2.120	0.370	0.737			2.149	0.370	0.797		
Fe3–CX	1.959	1.650	0.370	0.434	2.530	0.530	1.689	0.370	0.482	**2.749**	-0.251
Fe4–S1A	2.302	2.120	0.370	0.611			2.149	0.370	0.661		
Fe4–S3A	2.261	2.120	0.370	0.683			2.149	0.370	0.739		
Fe4–S4A	2.282	2.120	0.370	0.645			2.149	0.370	0.698		
Fe4–CX	1.996	1.650	0.370	0.393	**2.333**	0.333	1.689	0.370	0.436	2.534	-0.466

Fe5–S1B	2.248	2.120	0.370	0.708			2.149	0.370	0.765		
Fe5–S3A	2.283	2.120	0.370	0.644			2.149	0.370	0.696		
Fe5–S4B	2.247	2.120	0.370	0.709			2.149	0.370	0.767		
Fe5–CX	2.018	1.650	0.370	0.370	2.431	0.431	1.689	0.370	0.411	**2.640**	-0.360
Fe6–S1B	2.227	2.120	0.370	0.749			2.149	0.370	0.810		
Fe6–S3A	2.224	2.120	0.370	0.755			2.149	0.370	0.817		
Fe6–C2	2.031	1.650	0.370	0.357			1.689	0.370	0.397		
Fe6–C1	1.917	1.650	0.370	0.486			1.689	0.370	0.540		
Fe6–CX	2.063	1.650	0.370	0.328	2.674	0.674	1.689	0.370	0.364	**2.927**	-0.073
Fe7–S3B	2.241	2.120	0.370	0.721			2.149	0.370	0.780		
Fe7–S4B	2.244	2.120	0.370	0.715			2.149	0.370	0.774		
Fe7–S5A	2.194	2.120	0.370	0.819			2.149	0.370	0.885		
Fe7–CX	1.979	1.650	0.370	0.411	2.666	0.666	1.689	0.370	0.457	**2.896**	-0.104

Table S6 The bond valence analyses for irons in FeMo-cofactor (2) from MoFe protein 7JRF which coordinated with double CO on Fe6 with resolution of 1.33 Å.

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	2.295	2.120	0.370	0.623			2.149	0.370	0.674		
Fe1–S2A	2.249	2.120	0.370	0.706			2.149	0.370	0.763		
Fe1–S4A	2.286	2.120	0.370	0.638			2.149	0.370	0.691		
Fe1–SG	2.270	2.120	0.370	0.667	2.634	0.634	2.149	0.370	0.721	**2.849**	-0.151
Fe2–S1A	2.235	2.120	0.370	0.733			2.149	0.370	0.793		
Fe2–S2A	2.220	2.120	0.370	0.763			2.149	0.370	0.825		
Fe2–C	1.900	1.470	0.370	0.313			1.689	0.370	0.565		
Fe2–CX	1.989	1.650	0.370	0.400	2.405	0.405	1.689	0.370	0.444	**2.628**	-0.372
Fe3–S2A	2.271	2.120	0.370	0.665			2.149	0.370	0.719		
Fe3–S4A	2.249	2.120	0.370	0.706			2.149	0.370	0.763		
Fe3–S5A	2.222	2.120	0.370	0.759			2.149	0.370	0.821		
Fe3–CX	1.975	1.650	0.370	0.415	2.545	0.545	1.689	0.370	0.462	**2.765**	-0.235
Fe4–S1A	2.301	2.120	0.370	0.613			2.149	0.370	0.663		
Fe4–S3A	2.239	2.120	0.370	0.725			2.149	0.370	0.784		
Fe4–S4A	2.285	2.120	0.370	0.640			2.149	0.370	0.692		
Fe4–CX	1.991	1.650	0.370	0.398	**2.376**	0.376	1.689	0.370	0.442	2.582	-0.418

Fe5–S1B	2.265	2.120	0.370	0.676			2.149	0.370	0.731		
Fe5–S3A	2.287	2.120	0.370	0.637			2.149	0.370	0.689		
Fe5–S4B	2.249	2.120	0.370	0.706			2.149	0.370	0.763		
Fe5–CX	1.996	1.650	0.370	0.393	2.411	0.411	1.689	0.370	0.436	**2.619**	-0.381
Fe6–S1B	2.226	2.120	0.370	0.751			2.149	0.370	0.812		
Fe6–S3B	2.223	2.120	0.370	0.757			2.149	0.370	0.819		
Fe6–C1	1.931	1.650	0.370	0.468			1.689	0.370	0.520		
Fe6–C2	1.930	1.650	0.370	0.469			1.689	0.370	0.521		
Fe6–CX	2.088	1.650	0.370	0.306	2.751	0.751	1.689	0.370	0.340	**3.012**	0.012
Fe7–S3B	2.254	2.120	0.370	0.696			2.149	0.370	0.753		
Fe7–S4B	2.210	2.120	0.370	0.784			2.149	0.370	0.848		
Fe7–S5A	2.212	2.120	0.370	0.780			2.149	0.370	0.843		
Fe7–CX	1.973	1.650	0.370	0.418	2.678	0.678	1.689	0.370	0.464	**2.909**	-0.091

Table S7 The bond valence analyses for irons in FeMo-cofactor (1) from MoFe protein 6UG0 which coordinated with single N_2 between Fe2 and Fe6 with resolution of 1.83 Å..

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	2.297	2.120	0.370	0.620			2.149	0.370	0.670		
Fe1–S2A	2.244	2.120	0.370	0.715			2.149	0.370	0.774		
Fe1–S4A	2.264	2.120	0.370	0.678			2.149	0.370	0.733		
Fe1–SG	2.234	2.120	0.370	0.735	2.747	0.747	2.149	0.370	0.795	**2.971**	-0.029
Fe2–S1A	2.277	2.120	0.370	0.654			2.149	0.370	0.708		
Fe2–S2A	2.228	2.120	0.370	0.747			2.149	0.370	0.808		
Fe2–N6A	1.750	1.769	0.370	1.053			1.815	0.370	1.192		
Fe2–CX	2.015	1.650	0.370	0.373	2.827	0.827	1.689	0.370	0.414	**3.122**	0.122
Fe3–S2A	2.293	2.120	0.370	0.627			2.149	0.370	0.678		
Fe3–S4A	2.280	2.120	0.370	0.649			2.149	0.370	0.702		
Fe3–S5A	2.195	2.120	0.370	0.817			2.149	0.370	0.883		
Fe3–CX	1.969	1.650	0.370	0.422	2.514	0.514	1.689	0.370	0.469	**2.732**	-0.268
Fe4–S1A	2.308	2.120	0.370	0.602			2.149	0.370	0.651		
Fe4–S3A	2.219	2.120	0.370	0.765			2.149	0.370	0.828		
Fe4–S4A	2.279	2.120	0.370	0.651			2.149	0.370	0.704		
Fe4–CX	2.033	1.650	0.370	0.355	**2.373**	0.373	1.689	0.370	0.395	2.577	-0.423

Fe5–S1B	2.257	2.120	0.370	0.691			2.149	0.370	0.747		
Fe5–S3A	2.255	2.120	0.370	0.694			2.149	0.370	0.751		
Fe5–S4B	2.254	2.120	0.370	0.696			2.149	0.370	0.753		
Fe5–CX	1.987	1.650	0.370	0.402	2.483	0.483	1.689	0.370	0.447	**2.698**	-0.302
Fe6–S1B	2.250	2.120	0.370	0.704			2.149	0.370	0.761		
Fe6–S3A	2.249	2.120	0.370	0.706			2.149	0.370	0.763		
Fe6–N6B	2.369	1.769	0.370	0.198			1.815	0.370	0.224		
Fe6–CX	1.996	1.650	0.370	0.393	**1.999**	-0.001	1.689	0.370	0.436	2.184	-0.816
Fe7–S3B	2.210	2.120	0.370	0.784			2.149	0.370	0.848		
Fe7–S4B	2.235	2.120	0.370	0.733			2.149	0.370	0.793		
Fe7–S5A	2.204	2.120	0.370	0.797			2.149	0.370	0.862		
Fe7–CX	2.003	1.650	0.370	0.385	2.699	0.699	1.689	0.370	0.428	**2.930**	-0.070

Table S8 The bond valence analyses for irons in FeMo-cofactor (2) from MoFe protein 6UG0 which coordinated with double N_2 with resolution of 1.83 Å.

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	2.294	2.120	0.370	0.625			2.149	0.370	0.676		
Fe1–S2A	2.259	2.120	0.370	0.687			2.149	0.370	0.743		
Fe1–S4A	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe1–SG	2.293	2.120	0.370	0.627	2.591	0.591	2.149	0.370	0.678	**2.802**	-0.198
Fe2–S1A	2.259	2.120	0.370	0.687			2.149	0.370	0.743		
Fe2–S2A	2.235	2.120	0.370	0.733			2.149	0.370	0.793		
Fe2–S2B	2.158	2.120	0.370	0.902			2.149	0.370	0.976		
Fe2–CX	2.031	1.650	0.370	0.357	2.679	0.679	1.689	0.370	0.397	**2.908**	-0.092
Fe3–S2A	2.259	2.120	0.370	0.687			2.149	0.370	0.743		
Fe3–S4A	2.217	2.120	0.370	0.769			2.149	0.370	0.832		
Fe3–N6A	2.143	1.769	0.370	0.364			1.815	0.370	0.412		
Fe3–CX	2.012	1.650	0.370	0.376	**2.196**	0.196	1.689	0.370	0.418	2.405	-0.595
Fe4–S1A	2.257	2.120	0.370	0.691			2.149	0.370	0.747		
Fe4–N6A	1.785	1.769	0.370	0.958			1.815	0.370	1.084		
Fe4–S4A	2.284	2.120	0.370	0.642			2.149	0.370	0.694		
Fe4–CX	1.995	1.650	0.370	0.394	2.684	0.684	1.689	0.370	0.437	**2.963**	-0.037
Fe5–S1B	2.291	2.120	0.370	0.630			2.149	0.370	0.681		

Fe5–N6A	2.136	1.769	0.370	0.371			1.815	0.370	0.420		
Fe5–S4B	2.281	2.120	0.370	0.647			2.149	0.370	0.700		
Fe5–CX	2.034	1.650	0.370	0.354	**2.002**	0.002	1.689	0.370	0.394	2.195	-0.805
Fe6–S1B	2.170	2.120	0.370	0.874			2.149	0.370	0.945		
Fe6–S3B	2.252	2.120	0.370	0.700			2.149	0.370	0.757		
Fe6–S2B	2.178	2.120	0.370	0.855			2.149	0.370	0.925		
Fe6–CX	2.007	1.650	0.370	0.381	2.809	0.809	1.689	0.370	0.423	**3.050**	0.050
Fe7–S3B	2.246	2.120	0.370	0.711			2.149	0.370	0.769		
Fe7–S4B	2.218	2.120	0.370	0.767			2.149	0.370	0.830		
Fe7–N6A	1.779	1.769	0.370	0.973			1.815	0.370	1.102		
Fe7–CX	1.993	1.650	0.370	0.396	2.848	0.848	1.689	0.370	0.440	**3.141**	0.141

Table S9 The bond valence analyses for irons in FeMo-cofactor (1) from MoFe protein 6UG0 with single N_2 refined as S atom with resolution of 1.83 Å.

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	2.260	2.120	0.370	0.685			2.149	0.370	0.741		
Fe1–S2A	2.245	2.120	0.370	0.713			2.149	0.370	0.771		
Fe1–S4A	2.273	2.120	0.370	0.661			2.149	0.370	0.715		
Fe1–SG	2.296	2.120	0.370	0.621	2.681	0.681	2.149	0.370	0.672	**2.900**	-0.100
Fe2–S1A	2.237	2.120	0.370	0.729			2.149	0.370	0.788		
Fe2–S2A	2.241	2.120	0.370	0.721			2.149	0.370	0.780		
Fe2–S2B	2.154	2.120	0.370	0.912			2.149	0.370	0.987		
Fe2–CX	2.040	1.650	0.370	0.349	2.711	0.711	1.689	0.370	0.387	**2.942**	-0.058
Fe3–S2A	2.348	2.120	0.370	0.540			2.149	0.370	0.584		
Fe3–S4A	2.229	2.120	0.370	0.745			2.149	0.370	0.806		
Fe3–N6A	2.200	2.120	0.370	0.806			2.149	0.370	0.871		
Fe3–CX	1.954	1.650	0.370	0.440	2.530	0.530	1.689	0.370	0.489	**2.749**	-0.251
Fe4–S1A	2.268	2.120	0.370	0.670			2.149	0.370	0.725		
Fe4–N6A	2.181	2.120	0.370	0.848			2.149	0.370	0.917		
Fe4–S4A	2.327	2.120	0.370	0.572			2.149	0.370	0.618		
Fe4–CX	2.024	1.650	0.370	0.364	2.454	0.454	1.689	0.370	0.404	**2.665**	-0.335
Fe5–S1B	2.241	2.120	0.370	0.721			2.149	0.370	0.780		

Fe5–N6A	2.219	2.120	0.370	0.765			2.149	0.370	0.828		
Fe5–S4B	2.313	2.120	0.370	0.594			2.149	0.370	0.642		
Fe5–CX	1.963	1.650	0.370	0.429	2.509	0.509	1.689	0.370	0.477	**2.726**	-0.274
Fe6–S1B	2.205	2.120	0.370	0.795			2.149	0.370	0.860		
Fe6–S3B	2.277	2.120	0.370	0.654			2.149	0.370	0.708		
Fe6–S2B	2.170	2.120	0.370	0.874			2.149	0.370	0.945		
Fe6–CX	1.995	1.650	0.370	0.394	2.716	0.716	1.689	0.370	0.437	**2.949**	-0.051
Fe7–S3B	2.198	2.120	0.370	0.810			2.149	0.370	0.876		
Fe7–S4B	2.216	2.120	0.370	0.771			2.149	0.370	0.834		
Fe7–N6A	2.250	2.120	0.370	0.704			2.149	0.370	0.761		
Fe7–CX	1.984	1.650	0.370	0.405	2.691	0.691	1.689	0.370	0.451	**2.922**	-0.078

Table S10 The bond valence analyses for irons in FeMo-cofactor (2) from MoFe protein 6UG0 with double N_2 refined as S atoms with resolution of 1.83 Å.

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	2.323	2.120	0.370	0.578			2.149	0.370	0.625		
Fe1–S2A	2.184	2.120	0.370	0.841			2.149	0.370	0.910		
Fe1–S4A	2.200	2.120	0.370	0.806			2.149	0.370	0.871		
Fe1–SG	2.240	2.120	0.370	0.723	2.947	0.947	2.149	0.370	0.782	**3.188**	0.188
Fe2–S1A	2.147	2.120	0.370	0.930			2.149	0.370	1.005		
Fe2–S2A	2.289	2.120	0.370	0.633			2.149	0.370	0.685		
Fe2–S2B	2.195	2.120	0.370	0.817			2.149	0.370	0.883		
Fe2–CX	2.059	1.650	0.370	0.331	2.711	0.711	1.689	0.370	0.368	**2.941**	-0.059
Fe3–S2A	2.291	2.120	0.370	0.630			2.149	0.370	0.681		
Fe3–S4A	2.194	2.120	0.370	0.819			2.149	0.370	0.885		
Fe3–N6A	2.267	2.120	0.370	0.672			2.149	0.370	0.727		
Fe3–CX	2.020	1.650	0.370	0.368	2.489	0.489	1.689	0.370	0.409	**2.702**	-0.298
Fe4–S1A	2.190	2.120	0.370	0.828			2.149	0.370	0.895		
Fe4–N6A	2.235	2.120	0.370	0.733			2.149	0.370	0.793		
Fe4–S4A	2.332	2.120	0.370	0.564			2.149	0.370	0.610		
Fe4–CX	2.020	1.650	0.370	0.368	2.492	0.492	1.689	0.370	0.409	**2.706**	-0.294
Fe5–S1B	2.311	2.120	0.370	0.597			2.149	0.370	0.645		

Fe5–N6A	2.182	2.120	0.370	0.846			2.149	0.370	0.915		
Fe5–S4B	2.227	2.120	0.370	0.749			2.149	0.370	0.810		
Fe5–CX	2.060	1.650	0.370	0.330	2.522	0.522	1.689	0.370	0.367	**2.737**	-0.263
Fe6–S1B	2.219	2.120	0.370	0.765			2.149	0.370	0.828		
Fe6–S3B	2.212	2.120	0.370	0.780			2.149	0.370	0.843		
Fe6–S2B	2.103	2.120	0.370	1.047			2.149	0.370	1.132		
Fe6–CX	2.004	1.650	0.370	0.384	2.976	0.976	1.689	0.370	0.427	**3.230**	0.230
Fe7–S3B	2.219	2.120	0.370	0.765			2.149	0.370	0.828		
Fe7–S4B	2.279	2.120	0.370	0.651			2.149	0.370	0.704		
Fe7–N6A	2.278	2.120	0.370	0.652			2.149	0.370	0.706		
Fe7–CX	1.998	1.650	0.370	0.390	2.459	0.459	1.689	0.370	0.434	**2.671**	-0.329

Table S11 The bond valence analyses for Mo atom in FeMo-cofactor (1) from MoFe protein 3U7Q with resolution of 1.00 Å.

Bond	r_{ij} (Å)	R_0 (Å)	B (Å)	Bval	Sum	Diff.
expected valence = +2						
Mo–O5	2.210	1.812	0.370	0.341		
Mo–O7	2.177	1.812	0.370	0.373		
Mo–N	2.347	1.948	0.370	0.340		
Mo–S1B	2.358	2.141	0.370	0.556		
Mo–S3B	2.371	2.141	0.370	0.537		
Mo–S4B	2.354	2.141	0.370	0.562	2.710	0.710
expected valence = +3						
Mo–O5	2.210	1.834	0.370	0.362		
Mo–O7	2.177	1.834	0.370	0.396		
Mo–N	2.347	1.972	0.370	0.363		
Mo–S1B	2.358	2.189	0.370	0.633		
Mo–S3B	2.371	2.189	0.370	0.611		
Mo–S4B	2.354	2.189	0.370	0.640	**3.006**	0.006
expected valence = +4						
Mo–O5	2.210	1.856	0.370	0.384		
Mo–O7	2.177	1.856	0.370	0.420		
Mo–N	2.347	1.996	0.370	0.387		
Mo–S1B	2.358	2.237	0.370	0.721		
Mo–S3B	2.371	2.237	0.370	0.696		
Mo–S4B	2.354	2.237	0.370	0.729	3.338	-0.662

Table S12 The bond valence analyses for Mo atom in FeMo-cofactor (2) from MoFe protein 3U7Q with resolution of 1.00 Å.

Bond	r_{ij} (Å)	R_0 (Å)	B (Å)	Bval	Sum	Diff.
expected valence = +2						
Mo–O5	2.193	1.812	0.370	0.357		
Mo–O7	2.164	1.812	0.370	0.386		
Mo–N	2.332	1.948	0.370	0.354		
Mo–S1B	2.347	2.141	0.370	0.573		
Mo–S3B	2.367	2.141	0.370	0.543		
Mo–S4B	2.354	2.141	0.370	0.562	2.776	0.776
expected valence = +3						
Mo–O5	2.193	1.834	0.370	0.379		
Mo–O7	2.164	1.834	0.370	0.410		
Mo–N	2.332	1.972	0.370	0.378		
Mo–S1B	2.347	2.189	0.370	0.652		
Mo–S3B	2.367	2.189	0.370	0.618		
Mo–S4B	2.354	2.189	0.370	0.640	**3.078**	0.078
expected valence = +4						
Mo–O6	2.193	1.856	0.370	0.402		
Mo–O7	2.164	1.856	0.370	0.435		
Mo–N	2.332	1.996	0.370	0.403		
Mo–S1B	2.347	2.237	0.370	0.743		
Mo–S3B	2.367	2.237	0.370	0.704		
Mo–S4B	2.354	2.237	0.370	0.729	3.416	-0.584

Table S13 The bond valence analyses for Mo atom in FeMo-cofactor (1) from MoFe protein 4TKV with resolution of 1.50 Å.

Bond	r_{ij} (Å)	R_0 (Å)	B (Å)	Bval	Sum	Diff.
expected valence = +2						
Mo–O6	2.166	1.812	0.370	0.384		
Mo–O7	2.218	1.812	0.370	0.334		
Mo–N	2.381	1.948	0.370	0.310		
Mo–S1B	2.323	2.141	0.370	0.611		
Mo–S3B	2.354	2.141	0.370	0.562		
Mo–S4B	2.336	2.141	0.370	0.590	2.792	0.792
expected valence = +3						
Mo–O6	2.166	1.834	0.370	0.408		
Mo–O7	2.218	1.834	0.370	0.354		
Mo–N	2.381	1.972	0.370	0.331		
Mo–S1B	2.323	2.189	0.370	0.696		
Mo–S3B	2.354	2.189	0.370	0.640		
Mo–S4B	2.336	2.189	0.370	0.672	**3.101**	0.101
expected valence = +4						
Mo–O6	2.166	1.856	0.370	0.433		
Mo–O7	2.218	1.856	0.370	0.376		
Mo–N	2.381	1.996	0.370	0.353		
Mo–S1B	2.323	2.237	0.370	0.793		
Mo–S3B	2.354	2.237	0.370	0.729		
Mo–S4B	2.336	2.237	0.370	0.765	3.449	-0.551

Table S14 The bond valence analyses for Mo atom in FeMo-cofactor (2) from MoFe protein 4TKV with resolution of 1.50 Å.

Bond	r_{ij} (Å)	R_0 (Å)	B (Å)	Bval	Sum	Diff.
expected valence = +2						
Mo–O5	2.195	1.812	0.370	0.355		
Mo–O7	2.190	1.812	0.370	0.360		
Mo–N	2.394	1.948	0.370	0.300		
Mo–S1B	2.343	2.141	0.370	0.579		
Mo–S3B	2.346	2.141	0.370	0.575		
Mo–S4B	2.327	2.141	0.370	0.605	2.774	0.774
expected valence = +3						
Mo–O5	2.195	1.834	0.370	0.377		
Mo–O7	2.190	1.834	0.370	0.382		
Mo–N	2.394	1.972	0.370	0.320		
Mo–S1B	2.343	2.189	0.370	0.660		
Mo–S3B	2.346	2.189	0.370	0.654		
Mo–S4B	2.327	2.189	0.370	0.689	**3.081**	0.081
expected valence = +4						
Mo–O6	2.195	1.856	0.370	0.400		
Mo–O7	2.190	1.856	0.370	0.405		
Mo–N	2.394	1.996	0.370	0.341		
Mo–S1B	2.343	2.237	0.370	0.751		
Mo–S3B	2.346	2.237	0.370	0.745		
Mo–S4B	2.327	2.237	0.370	0.784	3.426	-0.574

Table S15 The bond valence analyses for Mo atom in FeMo-cofactor (1) from MoFe protein 7JRF with resolution of 1.33 Å.

Bond	r_{ij} (Å)	R_0 (Å)	B (Å)	Bval	Sum	Diff.
expected valence = +2						
Mo–O6	2.191	1.812	0.370	0.359		
Mo–O7	2.238	1.812	0.370	0.316		
Mo–N	2.348	1.948	0.370	0.339		
Mo–S1B	2.339	2.141	0.370	0.586		
Mo–S3B	2.383	2.141	0.370	0.520		
Mo–S4B	2.363	2.141	0.370	0.549	2.669	0.669
expected valence = +3						
Mo–O6	2.191	1.834	0.370	0.381		
Mo–O7	2.238	1.834	0.370	0.336		
Mo–N	2.348	1.972	0.370	0.362		
Mo–S1B	2.339	2.189	0.370	0.667		
Mo–S3B	2.383	2.189	0.370	0.592		
Mo–S4B	2.363	2.189	0.370	0.625	**2.962**	-0.038
expected valence = +4						
Mo–O6	2.191	1.856	0.370	0.404		
Mo–O7	2.238	1.856	0.370	0.356		
Mo–N	2.348	1.996	0.370	0.386		
Mo–S1B	2.339	2.237	0.370	0.759		
Mo–S3B	2.383	2.237	0.370	0.674		
Mo–S4B	2.363	2.237	0.370	0.711	3.291	-0.709

Table S16 The bond valence analyses for Mo atom in FeMo-cofactor (2) from MoFe protein 7JRF with resolution of 1.33 Å.

Bond	r_{ij} (Å)	R_0 (Å)	B (Å)	Bval	Sum	Diff.
expected valence = +2						
Mo–O5	2.191	1.812	0.370	0.359		
Mo–O7	2.237	1.812	0.370	0.317		
Mo–N	2.360	1.948	0.370	0.328		
Mo–S1B	2.337	2.141	0.370	0.589		
Mo–S3B	2.373	2.141	0.370	0.534		
Mo–S4B	2.359	2.141	0.370	0.555	2.682	0.682
expected valence = +3						
Mo–O5	2.191	1.834	0.370	0.381		
Mo–O7	2.237	1.834	0.370	0.336		
Mo–N	2.360	1.972	0.370	0.350		
Mo–S1B	2.337	2.189	0.370	0.670		
Mo–S3B	2.373	2.189	0.370	0.608		
Mo–S4B	2.359	2.189	0.370	0.632	**2.978**	-0.022
expected valence = +4						
Mo–O6	2.191	1.856	0.370	0.404		
Mo–O7	2.237	1.856	0.370	0.357		
Mo–N	2.360	1.996	0.370	0.374		
Mo–S1B	2.337	2.237	0.370	0.763		
Mo–S3B	2.373	2.237	0.370	0.692		
Mo–S4B	2.359	2.237	0.370	0.719	3.310	-0.690

Table S17 The bond valence analyses for Mo atom in single N_2-bound FeMo-cofactor (1) from MoFe protein 6UG0 with resolution of 1.83 Å. The valences in bracket are not included in valence sum.

Bond	r_{ij} (Å)	R_0 (Å)	B (Å)	Bval	Sum	Diff.
expected valence = +2						
Mo–O6	2.727	1.812	0.370	(0.084)		
Mo–O7	2.357	1.812	0.370	0.229		
Mo–N	2.514	1.948	0.370	0.217		
Mo–S1B	2.330	2.141	0.370	0.600		
Mo–S3B	2.361	2.141	0.370	0.552		
Mo–S4B	2.380	2.141	0.370	0.524	**2.122**	0.122
expected valence = +3						
Mo–O6	2.727	1.834	0.370	(0.090)		
Mo–O7	2.357	1.834	0.370	0.243		
Mo–N	2.514	1.972	0.370	0.231		
Mo–S1B	2.330	2.189	0.370	0.683		
Mo–S3B	2.361	2.189	0.370	0.628		
Mo–S4B	2.380	2.189	0.370	0.597	2.383	-0.617
expected valence = +4						
Mo–O6	2.727	1.856	0.370	(0.095)		
Mo–O7	2.357	1.856	0.370	0.258		
Mo–N	2.514	1.996	0.370	0.247		
Mo–S1B	2.330	2.237	0.370	0.778		
Mo–S3B	2.361	2.237	0.370	0.715		
Mo–S4B	2.380	2.237	0.370	0.679	2.677	-1.323

Table S18 The bond valence analyses for Mo atom in double N_2-bound FeMo-cofactor (2) from MoFe protein 6UG0 with resolution of 1.83 Å. The valences in bracket are not included in valence sum.

Bond	r_{ij} (Å)	R_0 (Å)	B (Å)	Bval	Sum	Diff.
expected valence = +2						
Mo–O5	2.323	1.812	0.370	0.251		
Mo–O7	2.736	1.812	0.370	(0.082)		
Mo–N	2.361	1.948	0.370	0.328		
Mo–S1B	2.380	2.141	0.370	0.524		
Mo–S3B	2.331	2.141	0.370	0.598		
Mo–S4B	2.361	2.141	0.370	0.552	**2.084**	0.084
expected valence = +3						
Mo–O5	2.323	1.834	0.370	0.267		
Mo–O7	2.736	1.834	0.370	(0.087)		
Mo–N	2.361	1.972	0.370	0.349		
Mo–S1B	2.380	2.189	0.370	0.597		
Mo–S3B	2.331	2.189	0.370	0.681		
Mo–S4B	2.361	2.189	0.370	0.628	2.343	-0.657
expected valence = +4						
Mo–O6	2.323	1.856	0.370	0.283		
Mo–O7	2.736	1.856	0.370	(0.093)		
Mo–N	2.361	1.996	0.370	0.373		
Mo–S1B	2.380	2.237	0.370	0.679		
Mo–S3B	2.331	2.237	0.370	0.776		
Mo–S4B	2.361	2.237	0.370	0.715	2.636	-1.364

Table S19 The bond valence analyses for Mo atom in FeMo-cofactor (1) from MoFe protein 6UG0 with single N_2 refined as S atom with resolution of 1.83 Å.[1]

Bond	r_{ij} (Å)	R_0 (Å)	B (Å)	Bval	Sum	Diff.
expected valence = +2						
Mo–O6	2.163	1.812	0.370	0.387		
Mo–O7	2.129	1.812	0.370	0.425		
Mo–N	2.266	1.948	0.370	0.423		
Mo–S1B	2.367	2.141	0.370	0.543		
Mo–S3B	2.376	2.141	0.370	0.530		
Mo–S4B	2.387	2.141	0.370	0.514	2.822	0.822
expected valence = +3						
Mo–O6	2.163	1.834	0.370	0.411		
Mo–O7	2.129	1.834	0.370	0.451		
Mo–N	2.266	1.972	0.370	0.452		
Mo–S1B	2.367	2.189	0.370	0.618		
Mo–S3B	2.376	2.189	0.370	0.603		
Mo–S4B	2.387	2.189	0.370	0.586	**3.120**	0.120
expected valence = +4						
Mo–O6	2.163	1.856	0.370	0.436		
Mo–O7	2.129	1.856	0.370	0.478		
Mo–N	2.266	1.996	0.370	0.482		
Mo–S1B	2.367	2.237	0.370	0.704		
Mo–S3B	2.376	2.237	0.370	0.687		
Mo–S4B	2.387	2.237	0.370	0.667	3.454	-0.546

Table S20 The bond valence analyses for Mo atom in FeMo-cofactor (2) from MoFe protein 6UG0 with double N_2 refined as S atoms with resolution of 1.83 Å.[1]

Bond	r_{ij} (Å)	R_0 (Å)	B (Å)	Bval	Sum	Diff.
expected valence = +2						
Mo–O6	2.104	1.812	0.370	0.454		
Mo–O7	2.108	1.812	0.370	0.449		
Mo–N	2.299	1.948	0.370	0.387		
Mo–S1B	2.425	2.141	0.370	0.464		
Mo–S3B	2.321	2.141	0.370	0.615		
Mo–S4B	2.396	2.141	0.370	0.502	2.872	0.872
expected valence = +3						
Mo–O6	2.104	1.834	0.370	0.482		
Mo–O7	2.108	1.834	0.370	0.477		
Mo–N	2.299	1.972	0.370	0.413		
Mo–S1B	2.425	2.189	0.370	0.528		
Mo–S3B	2.321	2.189	0.370	0.700		
Mo–S4B	2.396	2.189	0.370	0.572	**3.172**	0.172
expected valence = +4						
Mo–O6	2.104	1.856	0.370	0.512		
Mo–O7	2.108	1.856	0.370	0.506		
Mo–N	2.299	1.996	0.370	0.441		
Mo–S1B	2.425	2.237	0.370	0.602		
Mo–S3B	2.321	2.237	0.370	0.797		
Mo–S4B	2.396	2.237	0.370	0.651	3.508	-0.492

Table S21 The assumed bond valence analyses of Mo atom in 6UG0 if we replace the Mo–O distances by the corresponding bond distances of FeMo-cofactor in 3U7Q、4TKV、7JRF、1H1L and Mo^{3+} inorganic complex.

Bond	r_{ij} (Å)	R_0 (Å)	B (Å)	Bval	Sum	Diff.
expected valence = +3 (Mo–O distances substituted by data in 3U7Q)						
Mo–O5	2.193	1.834	0.370	0.379		
Mo–O7	2.164	1.834	0.370	0.410		
Mo–N	2.514	1.972	0.370	0.231		
Mo–S1B	2.330	2.189	0.370	0.683		
Mo–S3B	2.361	2.189	0.370	0.628		
Mo–S4B	2.380	2.189	0.370	0.597	**2.928**	-0.072
Mo–O5	2.210	1.834	0.370	0.362		
Mo–O7	2.177	1.834	0.370	0.396		
Mo–N	2.361	1.972	0.370	0.349		
Mo–S1B	2.380	2.189	0.370	0.597		
Mo–S3B	2.331	2.189	0.370	0.681		
Mo–S4B	2.361	2.189	0.370	0.628	**3.013**	0.013
expected valence = +3 (Mo–O distances substituted by data in 4TKV)						
Mo–O5	2.166	1.834	0.370	0.408		
Mo–O7	2.218	1.834	0.370	0.354		
Mo–N	2.514	1.972	0.370	0.231		
Mo–S1B	2.330	2.189	0.370	0.683		
Mo–S3B	2.361	2.189	0.370	0.628		
Mo–S4B	2.380	2.189	0.370	0.597	**2.901**	-0.099
Mo–O5	2.195	1.834	0.370	0.377		
Mo–O7	2.190	1.834	0.370	0.382		
Mo–N	2.361	1.972	0.370	0.349		
Mo–S1B	2.380	2.189	0.370	0.597		
Mo–S3B	2.331	2.189	0.370	0.681		
Mo–S4B	2.361	2.189	0.370	0.628	**3.015**	0.015

expected valence = +3 (Mo–O distances substituted by data in 7JRF)

Mo–O5	2.191	1.834	0.370	0.381		
Mo–O7	2.237	1.834	0.370	0.336		
Mo–N	2.514	1.972	0.370	0.231		
Mo–S1B	2.330	2.189	0.370	0.683		
Mo–S3B	2.361	2.189	0.370	0.628		
Mo–S4B	2.380	2.189	0.370	0.597	**2.857**	-0.143

Mo–O5	2.191	1.834	0.370	0.381		
Mo–O7	2.238	1.834	0.370	0.336		
Mo–N	2.361	1.972	0.370	0.349		
Mo–S1B	2.380	2.189	0.370	0.597		
Mo–S3B	2.331	2.189	0.370	0.681		
Mo–S4B	2.361	2.189	0.370	0.628	**2.972**	-0.028

expected valence = +3 (Mo–O distances substituted by data in 1H1L)

Mo–O5	2.269	1.834	0.370	0.309		
Mo–O7	2.253	1.834	0.370	0.322		
Mo–N	2.514	1.972	0.370	0.231		
Mo–S1B	2.330	2.189	0.370	0.683		
Mo–S3B	2.361	2.189	0.370	0.628		
Mo–S4B	2.380	2.189	0.370	0.597	**2.770**	-0.230

Mo–O5	2.312	1.834	0.370	0.275		
Mo–O7	2.251	1.834	0.370	0.324		
Mo–N	2.361	1.972	0.370	0.349		
Mo–S1B	2.380	2.189	0.370	0.597		
Mo–S3B	2.331	2.189	0.370	0.681		
Mo–S4B	2.361	2.189	0.370	0.628	**2.854**	-0.146

expected valence = +3 (Mo–O distances substituted by average Mo^{3+}–O in inorganic complex)

Mo–O5	2.165	1.834	0.370	0.409		
Mo–O7	2.153	1.834	0.370	0.422		
Mo–N	2.514	1.972	0.370	0.231		

Mo–S1B	2.330	2.189	0.370	0.683		
Mo–S3B	2.361	2.189	0.370	0.628		
Mo–S4B	2.380	2.189	0.370	0.597	**2.970**	-0.030
Mo–O5	2.165	1.834	0.370	0.409		
Mo–O7	2.153	1.834	0.370	0.422		
Mo–N	2.361	1.972	0.370	0.349		
Mo–S1B	2.380	2.189	0.370	0.597		
Mo–S3B	2.331	2.189	0.370	0.681		
Mo–S4B	2.361	2.189	0.370	0.628	**3.087**	0.087

Table S22 The Mo–O (α-alkoxy/α-hydroxy) and Mo–O (α-carboxy) distances (Å) of molybdenum α-hydroxycarboxylate complexes for Mo^{n+}–O linear fitting.

Mo α-hydroxycarboxylate complex	Mo–O (α-alkoxy/α-hydroxy)		Mo–O (α–Carboxy)	
Mo^0		H^a/O_t^b		O_t
$(Et_4N)_3[(Hcit)Mo(CO)_3]$[2]		2.230(2) (H)	2.229(2)	
$(Et_4N)_2[(Hmal)Mo(CO)_3]$[2]		2.286(3) (H)	2.255(3)	
Average		**2.258**	**2.242**	
Mo^{4+}		H/O_t		O_t
$[Mo_2O(Hcit)_2(tpy)_2]\cdot 3H_2O$[3]	1.966(2)		2.113(2)	
	1.978(2)		2.097(2)	
$Na_2[Mo_3SO_3(R,S\text{-lact})_3(im)_3]\cdot 10H_2O$[4]	1.994(6)		2.135(6)	
	2.003(6)		2.131(6)	
	1.999(7)		2.133(6)	
$[Mo_3S_4(PPh_3)_3(Hlac)_2(lac)]$[5]	2.092(3)	2.228(4) (H)	2.155(4)	
		2.179(4) (H)	2.083(4)	
			2.080(4)	
$Na_2[Mo_3(\mu_3\text{–}S)(\mu_2\text{–}O)_3(glyc)_3(2\text{-}mim)_3]\cdot 1.5H_2O$[6]	1.991(6)		2.171(6)	
	2.001(6)		2.160(6)	
	2.011(5)		2.187(5)	
	2.011(5)		2.173(5)	
$(4\text{-}Hmim)_6[Mo_3(\mu_3\text{–}S)(\mu_2\text{–}O)_3(glyc)_3(4\text{-}mim)_3]_2[MoO_2(glyc)_2]$[6]	2.017(4)		2.140(4)	
	2.003(4)		2.141(4)	
	2.014(4)		2.157(5)	
	2.011(3)		2.125(3)	
	2.008(3)		2.120(4)	
	2.016(3)		2.145(4)	
$Na_3(4\text{-}Hmim)[Mo_3(\mu_3\text{–}S)(\mu_2\text{–}O)_3(SO_3)(glyc)_3(4\text{-}mim)]\cdot 8H_2O$[6]	2.027(2)		2.146(2)	
	1.994(2)		2.140(2)	
	2.028(2)		2.148(2)	
$[Mo_3SO_3(glyc)_2(im)_5]\cdot im\cdot H_2O$[4]	1.984(2)		2.123(2)	
Average	**2.007**	**2.204**	**2.137**	
Mo^{5+}		H/O_t		O_t
trans-$[(MoO)_2O(H_2homocit)_2(bpy)_2]_4\cdot H_2O$[7]	1.950		2.066	
	1.956		2.067	
$K_{2.5}Na_2NH_4[Mo_2O_2S_2(cit)_2]\cdot 5H_2O$[8]	2.028		2.135	
	2.013		2.124	
$(MeNC_5H_5)_4[Mo_4O_8(cit)_2]\cdot 2H_2O$[9]			2.137(2)	
$[(MoO)_2O(H_2cit)_2(bpy)_2]\cdot 4H_2O$[10]	1.976(3)		2.077(3)	
	1.987(3)		2.075(3)	
$K_4(NH_4)_2[Mo_2O_2S_2(cit)_2]\cdot 10H_2O$[11]		1.975(8) (O_t)	2.199(9)	
$K_5(NH_4)[Mo_2O_2S_2(cit)_2]\cdot CH_3OH\cdot 5H_2O$[12]		1.993 (O_t)	2.174	
		1.995 (O_t)	2.210	
$K_5[Mo_2O_2S_2(Hcit)(cit)]\cdot 6H_2O\cdot CH_3OH$		2.037 (O_t)	2.222	

[13]		1.970 (O_t)	2.182	
$Na_6[(Mo_2O_4)_3(mal)_4]\cdot 5H_2O$[4]	Bridged		2.113(11)	
trans-$[(MoO)_2O(lact)_2(bpy)_2]\cdot 3H_2O$[14]	1.941(6)		2.031(7)	
	1.965(5)		2.070(6)	
trans-$[(MoO)_2O(lact)_2(phen)_2]\cdot 4H_2O$	1.959(2)		2.065(2)	
[14]	1.954(2)		2.061(2)	
$[(MoO)_2O(glyc)_2(bpy)_2]\cdot 3H_2O$[14]	1.962(3)		2.077(4)	
	1.954(3)		2.056(4)	
$(PyH)_2[Mo_2O_4(glyc)_2Py_2]$[15]		2.183(2) (O_t)	2.092(2)	
$(PyH)_4[Mo_4O_8Cl_4(glyc)_2]\cdot 2EtOH$[15]	Bridged		2.117(3)	
$[Mo_4O_8(glyc)_2Py_4]$[15]	Bridged		2.046(3)	
$(NH_4)_6[Mo_2O_4(cit)_2]\cdot 3H_2O$[16]		2.016(4) (O_t)	2.152(3)	
Average	**1.970**	**2.024**	**2.111**	
Mo^{6+}		H/O_t		O_t
$(H_2tpy)_2[Mo^{VI}_2O_5(Hcit)_2]\cdot 7.5H_2O$[3]	1.953(3)			2.204(3)
	1.971(3)			2.231(3)
$K_5[(MoO_2)_4O_3(R,S$-	1.935(4)			2.194(5)
$Hhomocit)_2]Cl\cdot 5H_2O$[17]	1.957(5)			2.191(5)
$K_2(NH_4)_2[(MoO_2)_4O_3(R,S$-	1.955(4)			2.194(4)
$Hhomocit)_2]\cdot 6H_2O$[17]	1.929(4)			2.181(4)
$K_2[MoO_2(R,S\text{-}H_2homocit)_2]\cdot 2H_2O$[18]	1.961(1)			2.211(1)
	2.007(1)			2.206(1)
$K_2\{Mo^{IV}_3O_4(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot 3im$ $\cdot 4H_2O$[7]	Bridged		2.104(5) 2.097(4)	
$(Him)_2\{Mo^{IV}_3O_4(im)_3[Mo^{VI}O_3(Hcit)]_2\}$ $\cdot im\cdot 6H_2O$[7]	Bridged		2.103(4) 2.104(4)	
$\{(C_6H_5)_4P\}[MoO_2Cl(H_2cit)]$[9]	1.922(3)			2.204(3)
$(PyH)_2[MoO_2(H_2cit)_2]\cdot Py$[9]	1.940(2)			2.181(2)
	1.951(2)			2.211(2)
$(PyH)_4[\{MoO_2(Hcit)\}_2(\mu_2\text{–}O)]\cdot 2Py$[9]	1.984(1)			2.205(1)
$(PyH)_4[Mo_4O_{11}(Hcit)_2]\cdot 2H_2O\cdot 1/2CH_3O$ H[9]	1.984(3)			2.219(3)
	1.973(3)			2.255(3)
$(PyH)_6[Mo_4O_{11}(Hcit)_2]Cl_2\cdot H_2O\cdot 3/2CH$ $_3OH$[9]	1.967(5)			2.197(4)
	2.010(4)			2.188(4)
$K_4[MoO(O_2)_2(cit)]\cdot 4H_2O$[19]	1.971(2)			2.232(3)
$K_5[MoO(O_2)_2(Hcit)H(Hcit)(O_2)_2OMo]\cdot$ $6H_2O$[19]	2.034(2)			2.197(2)
$[Mo_4O_{11}(cit)_2](Me_3N(CH_2)_6NMe_3)_2\cdot 12$ H_2O[20]	1.969			2.216
$[(MoO_2)_2O(H_2cit)(phen)(H_2O)_2]\cdot H_2O$ [10]	1.943(5)			2.208(5)
$[MoO_2(H_2cit)]\cdot H_2O$[10]	1.907(6)			2.144(6)
$K_4[MoO_3(cit)]\cdot 2H_2O$[21]		2.051 (O_t)		2.237
$K_4[(MoO_2)_2O(Hcit)_2]\cdot 4H_2O$[21]	1.958			2.210

$K[(MoO_2)_2(OH)(H_2cit)_2]\cdot 4H_2O$[16]	1.953(5)			2.249(5)
$(NH_4)_2[MoO_2(H_2cit)_2]\cdot H_2O$[22]	1.986(1)			2.216(1)
	1.938(1)			2.195(1)
$(NH_4)_3[MoO_2(H_2cit)(Hcit)]\cdot H_2O$[22]	1.939(2)			2.197(2)
	1.937(2)			2.221(2)
$(NH_4)_5[MoO_2(Hcit)(cit)]\cdot 2.5H_2O$[22]	1.956(2)			2.228(2)
	1.956(2)			2.162(2)
$K_2(NH_4)_2[(MoO_2)_4O_3(Hcit)_2]\cdot 5H_2O$[23]	1.949(5)			2.215(5)
	1.977(5)			2.188(5)
$(NH_4)_5[(MoO_2)_4O_3(Hcit)(cit)]\cdot 3H_2O$[23]	1.931(4)			2.242(4)
	1.931(4)			2.188(4)
$K_2(NH_4)_4[(MoO_2)_4O_3(cit)_2]\cdot 7H_2O$[23]	1.954(2)			2.204(3)
	1.957(2)			2.211(3)
$K_2[(MoO_2)_2O(H_2cit)_2]\cdot 4H_2O$[23]	1.919(2)			2.178(3)
$(NH_4)_3[(MoO_2)_2O(H_2cit)(Hcit)]$ [23]	1.931(2)			2.168(2)
$(NH_4)_{14}\{[(MoO_2)_2O(Hcit)_2][(MoO_2)_2O($	1.977(2)			2.218(2)
$Hcit)(cit)]_2\}\cdot 14H_2O$[23]	1.948(2)			2.196(2)
	1.949(2)			2.211(2)
	1.953(2)			2.222(2)
	1.948(2)			2.212(2)
	1.977(2)			2.226(2)
$(NH_4)_6[(MoO_2)_2O(cit)_2]\cdot 3.5H_2O$[23]	1.937(2)			2.220(3)
	1.974(2)			2.204(2)
	1.980(2)			2.184(2)
	1.961(3)			2.240(3)
$(NH_4)_4[MoO_3(cit)]\cdot 2H_2O$[23]		2.054(1) (O_t)		2.213(2)
$K_6[\{MoO_2(cit)\}_2O]\cdot 2H_2O$[24]	1.952			2.215
$K_6[Mo_2O_5(cit)_2]\cdot 5H_2O$[25]	1.966			2.178
	1.981			2.209
$K_2Na_4[(MoO_2)_2O(cit)_2]\cdot 5H_2O$[26]	1.929			2.218
	1.958			2.196
$(Et_4N)[Mo^{VI}O_2Cl(H_2cit)]\cdot H_2O$[7]	1.931(4)			2.178(3)
$Na_2[MoO_2(H_2cit)_2]\cdot 3H_2O$[27]	1.953			2.190
	1.960			2.246
$Na_6[Mo_2O_5(cit)_2)]\cdot 10.5H_2O$[28]	1.955(2)			2.181(2)
	1.967(2)			2.229(2)
trans-$[(MoO)_2O(Hmal)_2(phen)_2]\cdot 4H_2O$	1.964(4)		2.072(4)	
[14]	1.958(4)		2.081(4)	
$(NH_4)_4Mo_4O_{11}(mal)_2)\cdot 6H_2O$[29]	1.999			2.208
$Cs_2[MoO_2(Hmal)_2]\cdot H_2O$[30]	1.935			2.242(H)
$[Et_4N]_2[Mo_2O_5(Hmal)_2(H_2O)_2]$[28]	1.989(4)			2.222(4)
$K_{2n}[MoO(O_2)_2(S\text{-Hmal})]_n\cdot nH_2O$[19]	2.011(4)			2.277(4)
$K_8[(MoO_2)_2O(R\text{-mal})_2][(MoO_2)_2O(S\text{-}$	1.926(3)			2.238(2)
$mal)_2]\cdot 4H_2O$[31]				

$(Him)_2K_6[(MoO_2)_4O_3$(*R*-mal)$_2][(MoO_2)_4O_3$(*S*-mal)$_2]\cdot 8H_2O$[31]	1.961(2)			2.188(2)
	1.963(2)			2.183(2)
$Na_3[MoO_2H$(*S*-mal)$_2]$[32]	1.935			2.181
trans-$[(MoO)_2O(Hmal)_2(bpy)_2]$[14]	1.950(4)			2.074(4)
$(NH_4)_4[(MoO_2)_4O_3(mal)_2]\cdot H_2O$[33]	2.225			2.511
$(NH_4)_4[(MoO_2)_4O_3$(*R*-mal)$_2]\cdot 6H_2O$[34]	1.925			2.227
$\{Na_2[MoO_2$(*S*-lact)$_2]\}_3\cdot 13H_2O$[35]	1.969(5)			2.201(5)
	1.947(4)			2.181(4)
	1.951(4)			2.206(4)
$K_6[(MoO_2)_8(glyc)_6(Hglyc)_2]\cdot 10H_2O$[35]	1.984(7)		2.075(6)	
			2.057(5)	
			2.061(5)	
$K_2[MoO_2(glyc)_2]\cdot H_2O$[35]	1.929(3)			2.202(2)
	1.953(2)			2.204(2)
MoO_2(glyc)(bpy) [14]	1.921(3)			2.133(3)
$(NH_4)_2[MoO(O_2)_2$(glyc)$]\cdot 0.5EtOH$[36]	1.974(2)			2.310(2)
	2.011(2)			2.211(2)
$K_2[MoO(O_2)$(glyc)$]\cdot 2H_2O$[37]	1.991			2.239
$\{(C_6H_5)_4P\}[MoO_2$(glyc)(Hglyc)$]$[15]	1.945(1)			2.271(4)
Average	**1.961**	**2.053**	**2.084**	**2.211**

[a](H) represents that the coordinated O was protonated. [b](O_t) means that the contraposition of coordinated O is terminal oxygen.

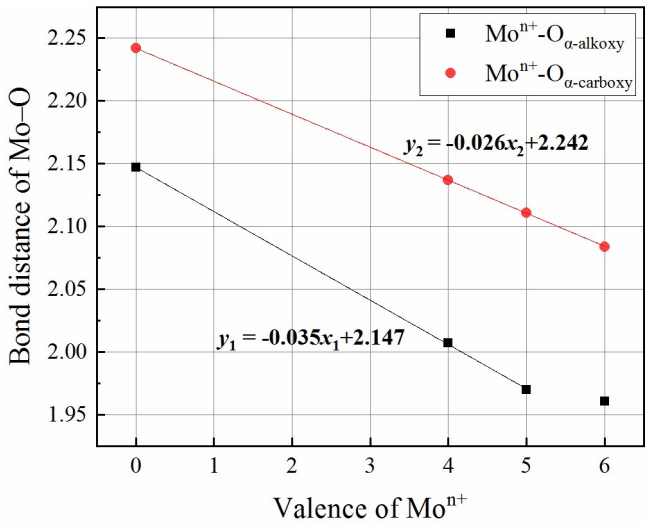

Figure S1 Plot and linear fit of average Mo^{n+}–O (α-alkoxy and α-carboxy) bond distances in molybdenum α-hydroxycarboxylates.

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