Supporting materials

Comparison of hydroxycarboxylato imidazole molybdenum(IV) complexes and nitrogenase protein structures : indirect evidence for the protonation of homocitrato FeMo-cofactor

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Figure S1. 2D layered structure of [(Mo_3SO_3) ($glyc)_2(im)_5$]·im·H_2O (**1**).
Figure S2. The 3D supramolecular are linked through hydrogen bonds in [(Mo_3SO_3) ($glyc)_2(im)_5$]·im·H_2O (**1**) viewed along *a* axis.
Figure S3. The 3D supramolecular are linked through hydrogen bonds in [(Mo_3SO_3) ($glyc)_2(im)_5$]·im·H_2O (**1**) viewed along *b* axis.
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Figure S12. UV-vis spectrum of $Na_6[(Mo_2O_4)_3(R,S\text{-mal})_4]$ $5H_2O$ (**4**).
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Figure S16. G–DTG curves of $Na_6[(Mo_2O_4)_3(R,S\text{-mal})_4]$ $5H_2O$ (**4**).
Table S1. Comparisons of selected bond distances (Å) for $[Mo_3SO_3(glyc)_2(im)_5]\cdot im\cdot H_2O$ (**1**), $Na_2[Mo_3SO_3(R,S\text{-lact})_3(im)_3]$ $10H_2O$ (**2**), $[Mo_6O_{10}(R,S\text{-lact})_2(im)_{10}]$ $16H_2O$ (**3**), *trans*-$[(MoO)_2O(glyc)_2(bpy)_2]$ $3H_2O$ (**5**),

trans-$[(MoO)_2O(glyc)_2(phen)_2]$ $5H_2O$ (**6**), *trans*-$[(MoO)_2O(glyc)_2(phen)_2]$ (**7**), $(PyH)_2[Mo_2O_4(glyc)_2Py_2]$ (**8**),[1] $(PyH)_4[Mo_4O_8Cl_4(glyc)_2]$ $2EtOH$ (**9**),[1] $[Mo_4O_8(glyc)_2Py_4]$ (**10**),[1] $K_6[(MoO_2)_8(glyc)_6(Hglyc)_2]$ $10H_2O$ (**11**),[2] $[Mo_3S_4(PPh_3)_3(Hlact)_2lact]$ (**15**),[3] *trans*-$[(MoO)_2O(R,S\text{-lact})_2(bpy)_2]$ $3H_2O$ (**16**), *trans*-$[(MoO)_2O(R,S\text{-lact})_2(phen)_2]$ $4H_2O$ (**17**), $Mo_3O_8(im)_4$ im H_2O (**20**),[4] $Mo_3O_8(im)_4$ H_2O (**21**),[4] $Mo_2O_6(im)_4$ (**22**),[5] *cis*-$Na_2[Mo_2O_4(ox)_2(im)_2]$ $4.5H_2O$ (**23**),[4] *cis*-$K_2[Mo_2O_4(ox)_2(im)_2]$ $3H_2O$ (**24**),[4] $K(Him)[Mo_3O_4(ox)_3(im)_3]$ $3H_2O$ (**25**),[4] $(4\text{-}MePyH)(H_3O)[Mo_3O_4(C_2O_4)_3(4\text{-}MePy)_3]$ H_2O (**26**),[6] $(MeNC_6H_{7)}(H_3O)[Mo_3O_4(C_2O_4)_3(4\text{-}MePy)_3]$ ½(4-MePy) (**27**),[6] $Na_2[Mo_3O_4((O_2CCH_2)_2NCH_3)_3]$ $7H_2O$ (**28**),[7] $[Mo_3O(OH)_3(Hnta)_3]$ Cl $3H_2O$ (**29**),[8] $Na_4[Mo_6O_8(EDTA)_3]$ $14H_2O$ (**30**),[9] $[Mo_3S_4(Clqn)_3(H_2O)_3]^+$ (**31**),[10] and $[Mo_6O_{10}(bpy)_4(Hnta)_2]$ $10H_2O$ (**37**)[11].

Table S2. Comparisons of selected bond distances (Å) for $[Mo_6O_{10}(R,S\text{-lact})_2(im)_{10}]$ $16H_2O$ (**3**), $K_6[(MoO_2)_8(glyc)_6(Hglyc)_2]$ $10H_2O$ (**11**)[2], $(PyH)_3[Mo_2O_4Cl_4(Hglyc)]$ $1/2CH_3CN$ (**38**)[1], $(PyH)_3[Mo_2O_4Br_4(Hglyc)]$ Pr^iOH (**39**),[1] and $K_2[(MoO_2)_2O(H_2cit)_2]\cdot 4H_2O$ (**40**)[12].

Table S3. Crystallographic data and structural refinements for complexes $[(Mo_3SO_3)(glyc)_2(im)_5]\cdot im\cdot H_2O$ (**1**), $Na_2[(Mo_3SO_3)(R,S\text{-lact})_3(im)_3]\cdot 10H_2O$ (**2**), $[(Mo_6O_{10})(R,S\text{-lact})_2(im)_{10}]\cdot 16H_2O$ (**3**), and $Na_6[(Mo_2O_4)_3(R,S\text{-mal})_4]$ $5H_2O$ (**4**).

Table S4. Selected bond distances (Å) and angles (°) for $[(Mo_3SO_3)(glyc)_2(im)_5]\cdot im\cdot H_2O$ (**1**).

Table S5. Selected bond distances (Å) and angles (°) for $Na_2[(Mo_3SO_3)(R,S\text{-lact})_3(im)_3]\cdot 10H_2O$ (**2**).

Table S6. Selected bond distances (Å) and angles (°) for $[(Mo_6O_{10})(R,S\text{-lact})_2(im)_{10}]\cdot 16H_2O$ (**3**).

Table S7. Selected bond distances (Å) and angles (°) for $Na_6[(Mo_2O_4)_3(R,S\text{-mal})_4]$ $5H_2O$ (**4**).

Table S8. Selected bond distances (Å) and angles (°) within the water layer in $Na_2[(Mo_3SO_3)(R,S\text{-lact})_3(im)_3]\cdot 10H_2O$ (**2**).

Table S9. Bond valence calculations for complexes $[(Mo_3SO_3)(glyc)_2(im)_5]\cdot im\cdot H_2O$ (**1**), $Na_2[(Mo_3SO_3)(R,S\text{-lact})_3(im)_3]\cdot 10H_2O$ (**2**), $[(Mo_6O_{10})(R,S\text{-lact})_2(im)_{10}]\cdot 16H_2O$ (**3**), and $Na_6[(Mo_2O_4)_3(R,S\text{-mal})_4]$ $5H_2O$ (**4**).

Table S10. The bond distances of Mo–$O_{\alpha\text{-alkoxy/hydroxy}}$, Mo–$O_{\alpha\text{-carboxy}}$ and C–$O_{\alpha\text{-alkoxy/hydroxy}}$ from FeMo-cofactors of MoFe-proteins in nitrogenases.

Figure S1. 2D layered structure of $[(Mo_3SO_3)\ (glyc)_2(im)_5]\cdot im\cdot H_2O$ (**1**).

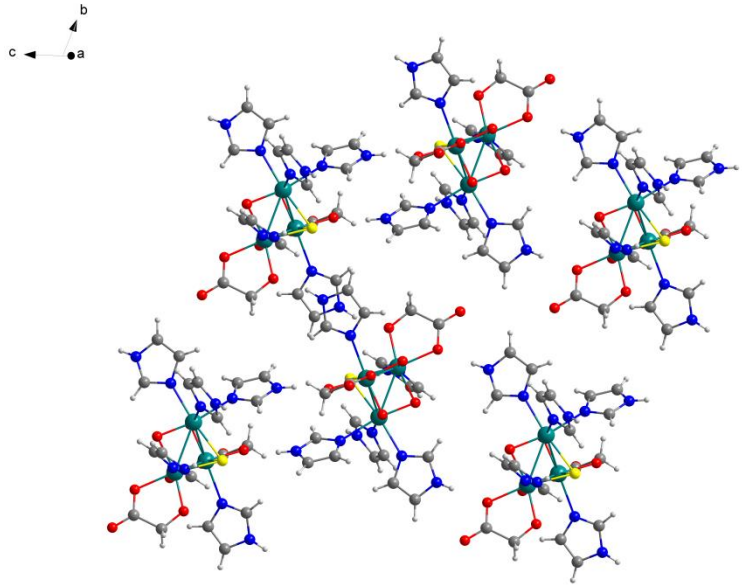

Figure S2. The 3D supramolecular are linked through hydrogen bonds in $[(Mo_3SO_3)\ (glyc)_2(im)_5]\cdot im\cdot H_2O$ (**1**) viewed along *a* axis.

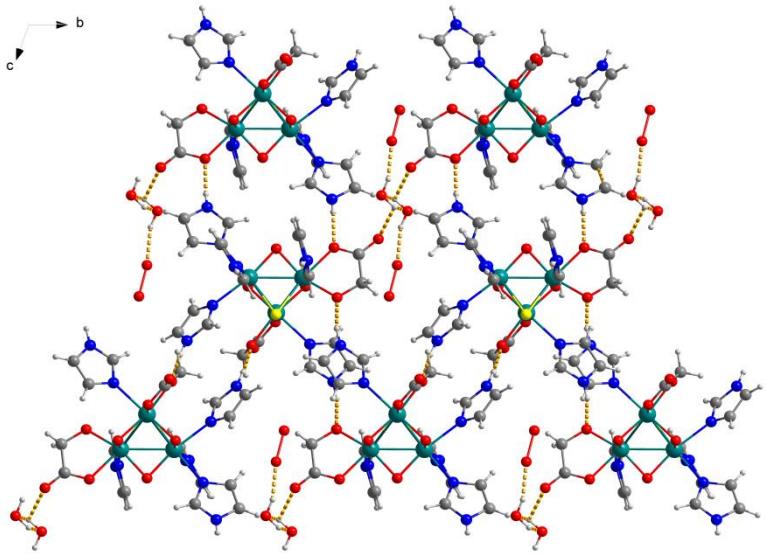

Figure S3. The 3D supramolecular are linked through hydrogen bonds in [(Mo_3SO_3)($glyc)_2(im)_5$]·im·H_2O (**1**) viewed along *b* axis.

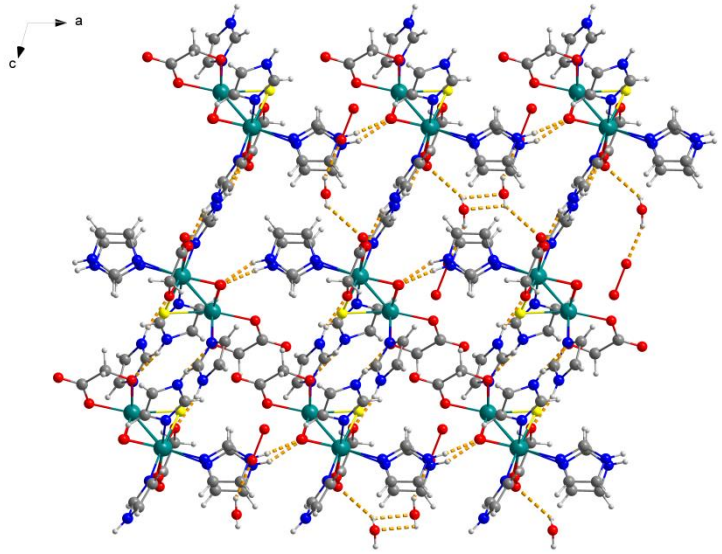

Figure S4. 2D layered structure of Na_2[(Mo_3SO_3)(*R*,*S*-lact)$_3$($im)_3$]·10H_2O (**2**).

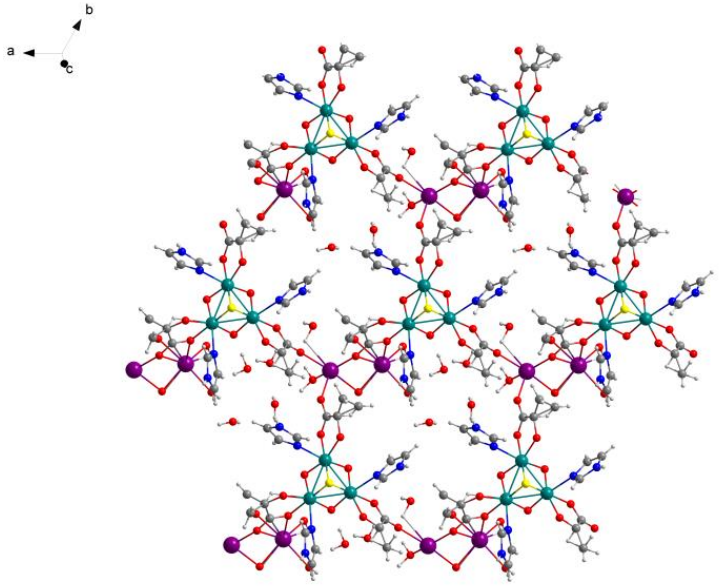

Figure S5. The 3D supramolecular are linked through hydrogen bonds in $Na_2[(Mo_3SO_3)(R,S\text{-lact})_3(im)_3]\cdot 10H_2O$ (**2**) viewed along *c* axis.

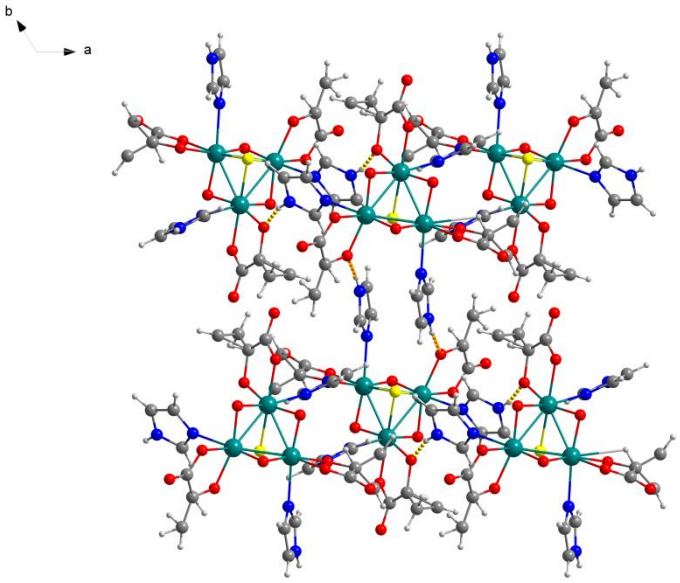

Figure S6. 2D layered structure of $[(Mo_6O_{10})(R,S\text{-lact})_2(im)_{10}]\cdot 16H_2O$ (**3**)

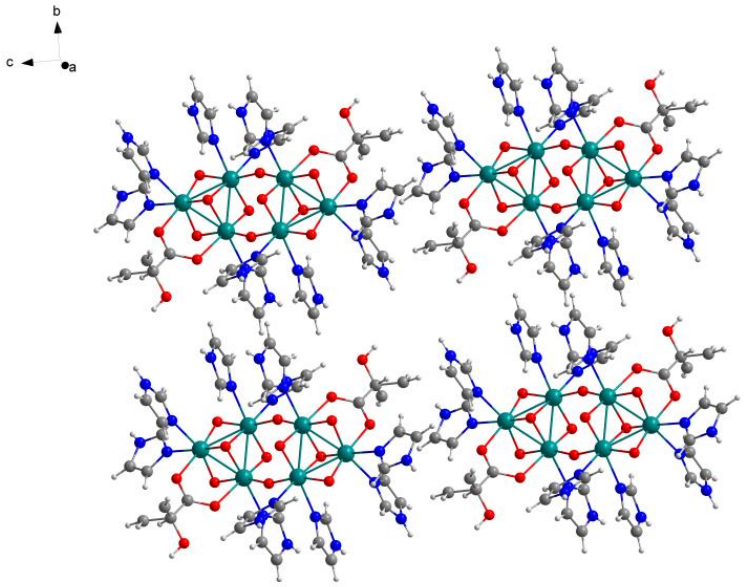

Figure S7. 3D water layers in $[(Mo_6O_{10})(R,S\text{-lact})_2(im)_{10}]\cdot 16H_2O$ (**3**).

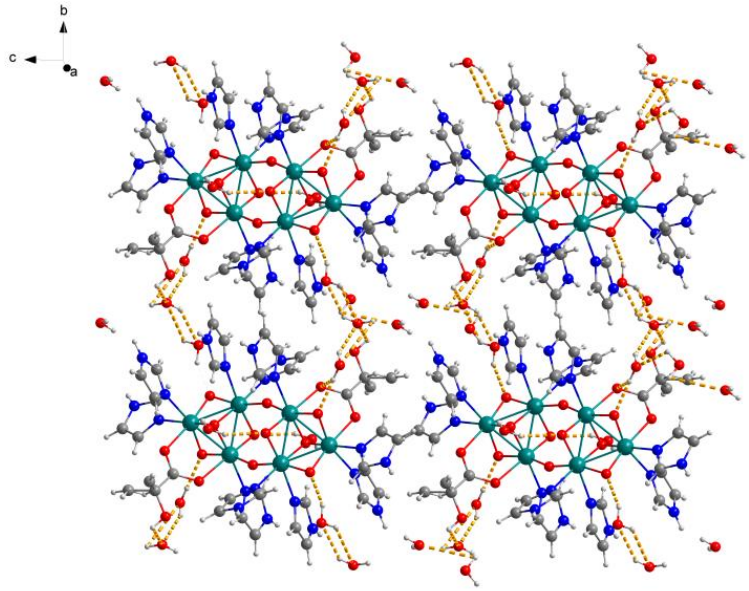

Figure S8. 2D layered structure of $Na_6[(Mo_2O_4)_3(R,S\text{-mal})_4]\ 5H_2O$ (**4**).

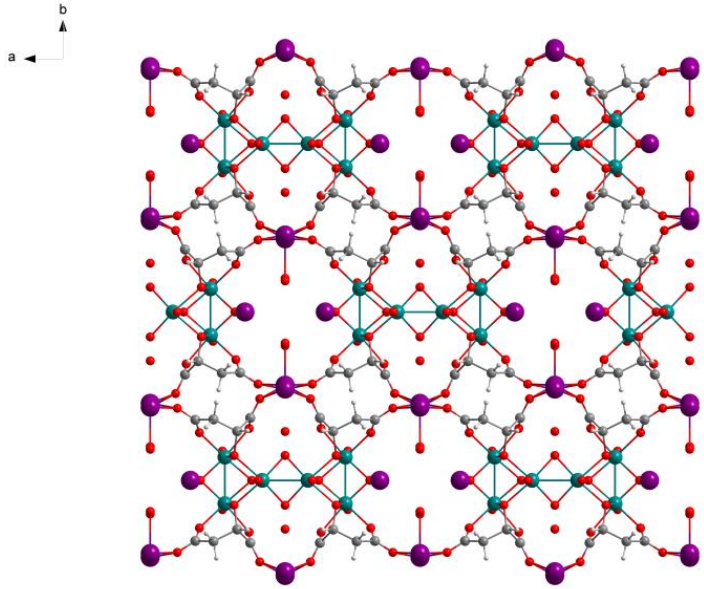

Figure S9. IR spectra of $[(Mo_3SO_3)(glyc)_2(im)_5]\cdot im\cdot H_2O$ (**1**), $Na_2[(Mo_3SO_3)(R,S\text{-lact})_3(im)_3]\cdot 10H_2O$ (**2**), and $[(Mo_6O_{10})(R,S\text{-lact})_2(im)_{10}]\cdot 16H_2O$ (**3**).

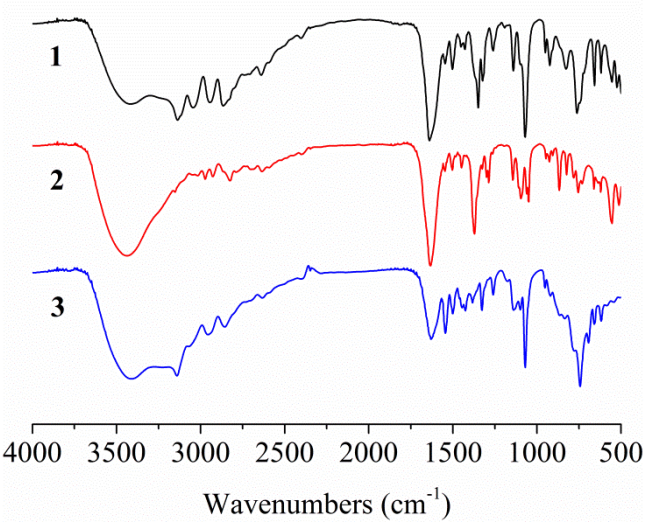

Figure S10. IR spectrum of $Na_6[(Mo_2O_4)_3(R,S\text{-mal})_4]\ 5H_2O$ (**4**).

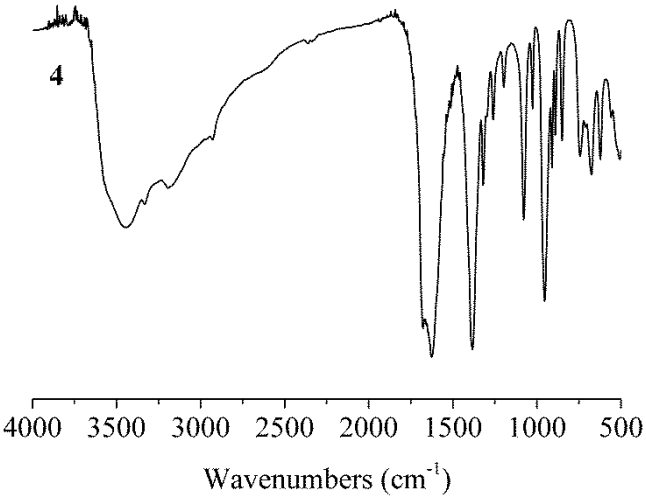

Figure S11. UV-vis spectra of $[(Mo_3SO_3)(glyc)_2(im)_5]\cdot im\cdot H_2O$ (**1**), $Na_2[(Mo_3SO_3)(R,S\text{-lact})_3(im)_3]\cdot 10H_2O$ (**2**), and $[(Mo_6O_{10})(R,S\text{-lact})_2(im)_{10}]\cdot 16H_2O$ (**3**).

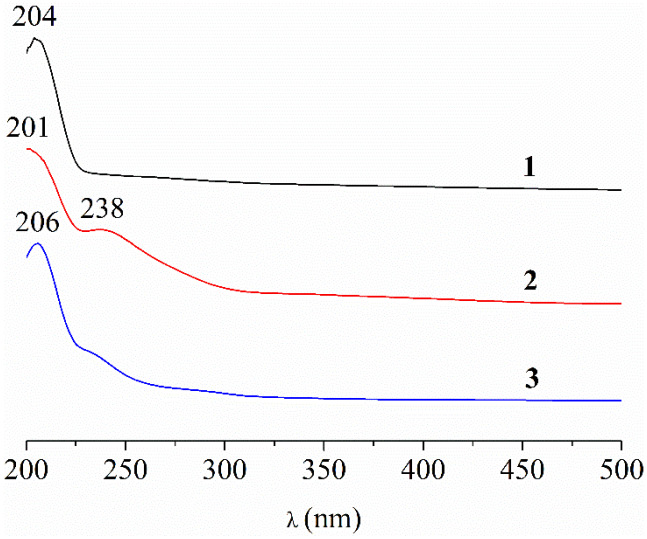

Figure S12. UV-vis spectrum of $Na_6[(Mo_2O_4)_3(R,S\text{-mal})_4]$ $5H_2O$ (**4**).

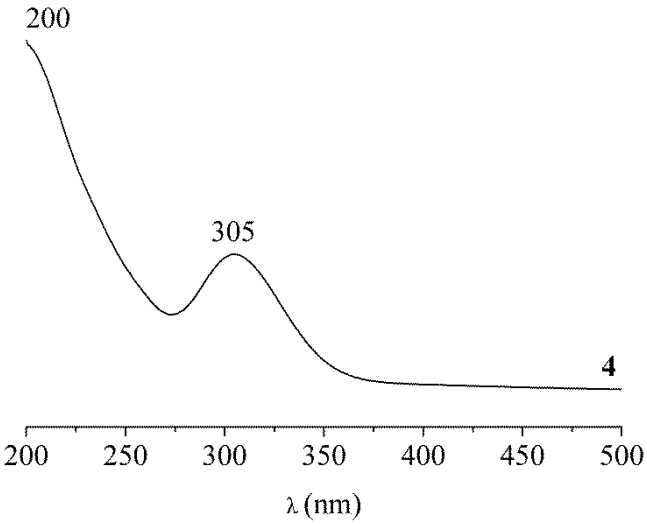

Figure S13. G–DTG curves of $[(Mo_3SO_3)\ (glyc)_2(im)_5]\cdot im\cdot H_2O$ (**1**).

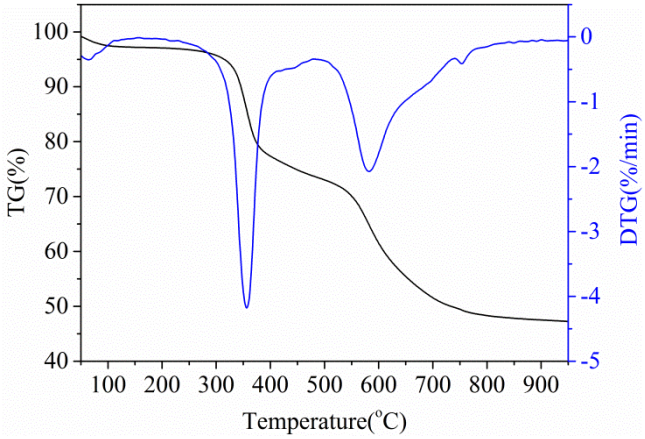

Figure S14. G–DTG curves of $Na_2[(Mo_3SO_3)(R,S\text{-lact})_3(im)_3]\cdot 10H_2O$ (**2**).

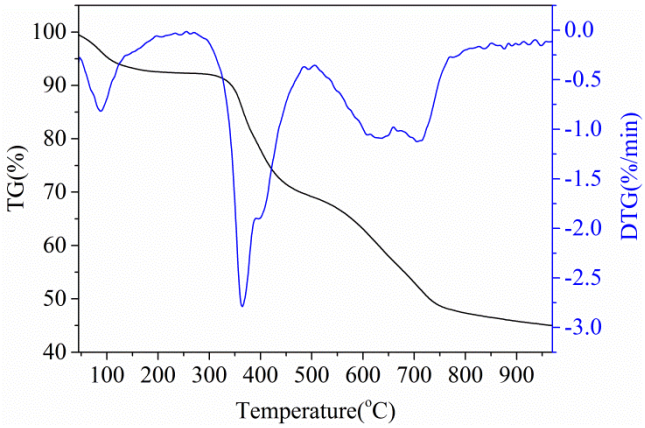

Figure S15. G–DTG curves of $[(Mo_6O_{10})(R,S\text{-lact})_2(im)_{10}]\cdot 16H_2O$ (**3**).

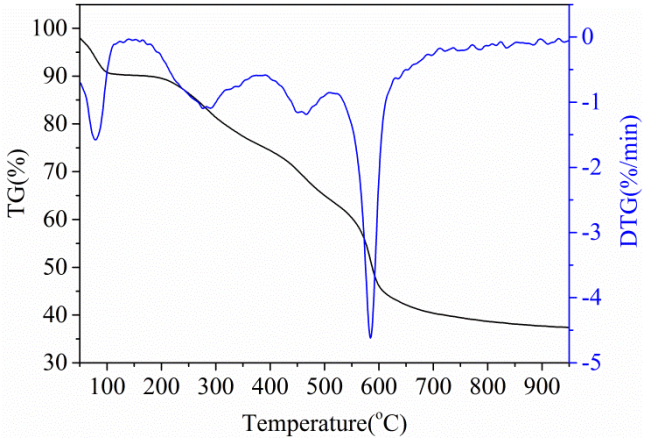

Figure S16. G–DTG curves of $Na_6[(Mo_2O_4)_3(R,S\text{-mal})_4]\ 5H_2O$ (**4**).

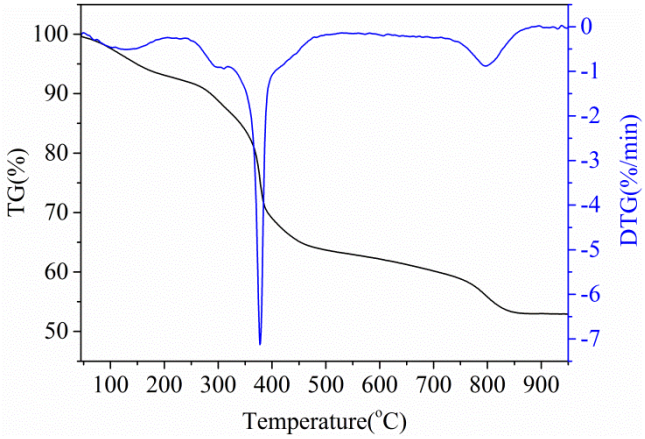

Table S1. Comparisons of selected bond distances (Å) for $[Mo_3SO_3(glyc)_2(im)_5]\cdot im\cdot H_2O$ (**1**), $Na_2[Mo_3SO_3(R,S\text{-lact})_3(im)_3]\cdot 10H_2O$ (**2**), $[Mo_6O_{10}(R,S\text{-lact})_2(im)_{10}]\cdot 16H_2O$ (**3**), *trans*-$[(MoO)_2O(glyc)_2(bpy)_2]\cdot 3H_2O$ (**5**), *trans*-$[(MoO)_2O(glyc)_2(phen)_2]\cdot 5H_2O$ (**6**), *trans*-$[(MoO)_2O(glyc)_2(phen)_2]$ (**7**), $(PyH)_2[Mo_2O_4(glyc)_2Py_2]$ (**8**),[1] $(PyH)_4[Mo_4O_8Cl_4(glyc)_2]\cdot 2EtOH$ (**9**),[1] $[Mo_4O_8(glyc)_2Py_4]$ (**10**),[1] $K_6[(MoO_2)_8(glyc)_6(Hglyc)_2]\cdot 10H_2O$ (**11**),[2] $[Mo_3S_4(PPh_3)_3(Hlact)_2lact]$ (**15**),[3] *trans*-$[(MoO)_2O(R,S\text{-lact})_2(bpy)_2]\cdot 3H_2O$ (**16**), *trans*-$[(MoO)_2O(R,S\text{-lact})_2(phen)_2]\cdot 4H_2O$ (**17**), $Mo_3O_8(im)_4\cdot im\cdot H_2O$ (**20**),[4] $Mo_3O_8(im)_4\cdot H_2O$ (**21**),[4] $Mo_2O_6(im)_4$ (**22**),[5] *cis*-$Na_2[Mo_2O_4(ox)_2(im)_2]\cdot 4.5H_2O$ (**23**),[4] *cis*-$K_2[Mo_2O_4(ox)_2(im)_2]\cdot 3H_2O$ (**24**),[4] $K(Him)[Mo_3O_4(ox)_3(im)_3]\cdot 3H_2O$ (**25**),[4] $(4\text{-}MePyH)(H_3O)[Mo_3O_4(C_2O_4)_3(4\text{-}MePy)_3]\cdot H_2O$ (**26**),[6] $(MeNC_6H_7)(H_3O)[Mo_3O_4(C_2O_4)_3(4\text{-}MePy)_3]\cdot ½(4\text{-}MePy)$ (**27**),[6] $Na_2[Mo_3O_4((O_2CCH_2)_2NCH_3)_3]\cdot 7H_2O$ (**28**),[7] $[Mo_3O(OH)_3(Hnta)_3]\cdot Cl\cdot 3H_2O$ (**29**),[8] $Na_4[Mo_6O_8(EDTA)_3]\cdot 14H_2O$ (**30**),[9] $[Mo_3S_4(Clqn)_3(H_2O)_3]^+$ (**31**),[10] and $[Mo_6O_{10}(bpy)_4(Hnta)_2]\cdot 10H_2O$ (**37**)[11].

Complexes(Mo^{n+})	Mo–μ_2-O/S	Mo–Mo
1(+4)	$1.929(2)_{av}$	$2.610(1)_{av}$
5(+5)	$1.871(3)_{av}$	
6(+5)	$1.861(3)_{av}$	
7(+5)	$1.864(2)_{av}$	
8[1](+5)	$1.937(2)_{av}$	2.559(1)
9[1](+5)	$1.935(3)_{av}$	2.612(1)
10[1](+5)	$1.926(3)_{av}$	2.588(1)
11[2](+5)	$1.930(6)_{av}$	$2.600(1)_{av}$
2(+4)	$1.936(6)_{av}$	$2.612(1)_{av}$
15[3](+4)	$2.296(1)_{av}$	$2.761(1)_{av}$
16(+5)	$1.865(6)_{av}$	
17(+5)	$1.865(2)_{av}$	
3(+4)	$1.905(4)_{av}$/$1.906(4)_{av}$/ $1.928(4)_{av}$/$2.002(4)_{av}$	$2.529(1)_{av}$
20[4](+5/6)	$1.947(4)_{av}$	2.573(1)
21[4](+5/6)	$1.952(4)_{av}$	2.573(1)
22[5](+6)	$1.940(3)_{av}$	
23[4](+5)	$1.938(3)_{av}$	2.560(1)
24[4](+5)	$1.940(3)_{av}$	2.548 (1)
25[4](+4)	$1.910(4)_{av}$	$2.494(1)_{av}$
26[6](+4)	$1.914(3)_{av}$	$2.499(5)_{av}$
27[6](+4)	$1.927(2)_{av}$	$2.503(3)_{av}$
28[7](+4)	$1.918(4)_{av}$	$2.495(1)_{av}$
29[8](+4)	$1.903(8)_{av}$	$2.482(1)_{av}$
30[9](+4)	$1.920(7)_{av}$	$2.506(1)_{av}$
31[10](+4)	$2.301(1)_{av}$	$2.766(1)_{av}$
37[11](+4)	$1.903(3)_{av}$/$1.932(3)_{av}$/ $2.002(3)_{av}$	$2.532(2)_{av}$

Table S2. Comparisons of selected bo/*nd distances (Å) for $[Mo_6O_{10}(R,S\text{-lact})_2(im)_{10}]\cdot 16H_2O$ (**3**), $K_6[(MoO_2)_8(glyc)_6(Hglyc)_2]\cdot 10H_2O$ (**11**)[2], $(PyH)_3[Mo_2O_4Cl_4(Hglyc)]\cdot 1/2CH_3CN$ (**38**)[1], $(PyH)_3[Mo_2O_4Br_4(Hglyc)]\cdot {}^{i}PrOH$ (**39**),[1] and $K_2[(MoO_2)_2O(H_2cit)_2]\cdot 4H_2O$ (**40**)[12]

Complexes(Mo^{n+})	Mo–$O_{\alpha\text{-carboxy}}$(C=O)	Mo–$O_{\alpha\text{-carboxy}}$(C–O)	C=$O_{\alpha\text{-carboxy}}$	C–$O_{\alpha\text{-carboxy}}$
38[1](+5)	2.389(2)	2.307(2)	1.260(4)	1.268(4)
39[1](+5)	2.373(3)	2.314(3)	1.258(5)	1.272(6)
11[2](+5)	2.318(6)	2.298(5)		
3(+4)	2.165(4)	2.201(4)	1.312(7)	1.324(7)
40[12](+6)	2.538(2)		1.227(5)	

Table S3. Crystallographic data and structural refinements for complexes $[(Mo_3SO_3)(glyc)_2(im)_5]\cdot im\cdot H_2O$ (**1**), $Na_2[(Mo_3SO_3)(R,S\text{-lact})_3(im)_3]\cdot 10H_2O$ (**2**), $[(Mo_6O_{10})(R,S\text{-lact})_2(im)_{10}]\cdot 16H_2O$ (**3**), and $Na_6[(Mo_2O_4)_3(R,S\text{-mal})_4]\ 5H_2O$ (**4**)

Identification code	**1**	**2**
Empirical formula	$C_{22}H_{38}Mo_3N_{12}O_{10}S$	$C_{18}H_{44}Mo_3N_6Na_2O_{22}S$
Formula weight	942.46	1062.45
Temperature/K	173.0	173.0
Crystal system	triclinic	triclinic
Space group	*P*-1	*P*-1
a/Å	8.6290(3)	12.4659(7)
b/Å	12.1305(4)	12.7032(7)
c/Å	17.0785(6)	14.8254(9)
α/°	109.173(3)	105.896(5)
β/°	104.625(3)	94.713(5)
γ/°	90.077(3)	119.364(6)
Volume/Å^3	1626.9(1)	1901.1(2)
Z	2	2
d_{calc}g/cm^3	1.924	1.856
μ/mm^{-1}	1.274	9.513
F(000)	844.0	1068.0
Crystal size/mm^3	0.3 × 0.2 × 0.04	0.28 × 0.28 × 0.02
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)
2θ range for data collection/ °	4.898 to 59.832	6.416 to 124.254
Index ranges	-11 ≤ h ≤ 12, -16 ≤ k ≤ 16, -23 ≤ l ≤ 22	-14 ≤ h ≤ 13, -11 ≤ k ≤ 14, -16 ≤ l ≤ 15
Reflections collected	25698	10608
Independent reflections	8418 [*R*int = 0.0413, *R*sigma = 0.0552]	5910 [R_{int} = 0.0538, R_{sigma} = 0.0727]
Data/restraints/parameters	8418/181/406	5910/119/520
Goodness–of–fit on F^2	1.019	1.123
Final *R* indexes [$I \geq 2\sigma(I)$]	*R*1 = 0.0388, *wR*2 = 0.0855	R_1 = 0.0686, wR_2 = 0.1790
Final *R* indexes [all data]	*R*1 = 0.0508, *wR*2 = 0.0913	R_1 = 0.0731, wR_2 = 0.1832
Largest diff. peak/hole / e Å^{-3}	1.00/-0.84	1.79/-1.40

Identification code	**3**	**4**
Empirical formula	$C_{36}H_{82}Mo_6N_{20}O_{32}$	$C_{16}H_{22}Mo_6Na_6O_{37}$

Formula weight	1882.85	1519.91
Temperature/K	173	173
Crystal system	triclinic	orthorhombic
Space group	*P*-1	*I*mm2
a/Å	10.6194(5)	15.0786(10)
b/Å	11.9177(5)	18.8242(10)
c/Å	14.7094(10)	7.2176(5)
α/°	90.197(4)	90
β/°	106.313(5)	90
γ/°	110.829(4)	90
Volume/Å^3	1658.78(16)	2048.7(2)
Z	1	2
d_{calc}g/cm^3	1.885	2.464
μ/mm^{-1}	1.200	16.317
F(000)	946.0	1364.0
Crystal size/mm^3	0.2 × 0.1 × 0.04	0.04 × 0.02 × 0.01
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)
2θ range for data collection/ °	4.304 to 50	7.512 to 124.37
Index ranges	-12 ≤ h ≤ 11, -14 ≤ k ≤ 13, -13≤ l ≤ 17	–17 ≤ h ≤ 16, –21 ≤ k ≤ 21, –8 ≤ l ≤ 5
Reflections collected	11292	5531
Independent reflections	5853 [R_{int} = 0.0453, R_{sigma} = 0.0794]	1451 [R_{int} = 0.0465, R_{sigma} = 0.0416]
Data/restraints/parameters	5853/419/364	1451/153/149
Goodness–of–fit on F^2	1.031	1.068
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0520, wR_2 = 0.1138	R_1 = 0.0546, wR_2 = 0.1513
Final *R* indexes [all data]	R_1 = 0.0689, wR_2 = 0.1199	R_1 = 0.0559, wR_2 = 0.1544
Largest diff. peak/hole / e Å^{-3}	1.15/-1.03	2.74/–1.16
Flack parameter		0.03(6)

Table S4. Selected bond distances (Å) and angles (°) for $[(Mo_3SO_3)(glyc)_2(im)_5]\cdot im\cdot H_2O$ (**1**).

Mo(1)–Mo(2)	2.6257(4)	Mo(2)–O(7)	1.988(2)
Mo(1)–Mo(3)	2.5980(4)	Mo(2)–O(8)	2.130(2)
Mo(1)–O(1)	1.942(2)	Mo(2)–N(3)	2.251(3)
Mo(1)–O(3)	1.926(2)	Mo(2)–S(1)	2.3604(8)
Mo(1)–O(4)	1.984(2)	Mo(3)–O(2)	1.925(2)
Mo(1)–O(5)	2.123(2)	Mo(3)–O(3)	1.916(2)
Mo(1)–N(1)	2.228(3)	Mo(3)–N(5)	2.236(3)
Mo(1)–S(1)	2.3433(8)	Mo(3)–N(7)	2.201(3)
Mo(2)–Mo(3)	2.6075(4)	Mo(3)–N(9)	2.198(3)
Mo(2)–O(1)	1.936(2)	Mo(3)–S(1)	2.3764(8)
Mo(2)–O(2)	1.927(2)		
Mo(2)–Mo(1)–Mo(3)	59.89(1)	N(3)–Mo(2)–S(1)	88.26(8)
O(1)–Mo(1)–Mo(2)	47.29(7)	S(1)–Mo(2)–Mo(1)	55.76(2)
O(1)–Mo(1)–Mo(3)	92.01(7)	S(1)–Mo(2)–Mo(3)	56.89(2)
O(1)–Mo(1)–O(3)	92.02(9)	Mo(1)–Mo(3)–Mo(2)	60.58(1)
O(1)–Mo(1)–O(4)	164.5(1)	O(2)–Mo(3)–Mo(1)	94.75(7)
O(1)–Mo(1)–O(5)	88.59(9)	O(2)–Mo(3)–Mo(2)	47.44(7)
O(1)–Mo(1)–N(1)	85.6(1)	O(2)–Mo(3)–O(3)	95.40(9)
O(1)–Mo(1)–S(1)	102.48(7)	O(2)–Mo(3)–N(5)	170.1(1)
O(3)–Mo(1)–Mo(2)	92.57(7)	O(2)–Mo(3)–N(7)	83.0(1)
O(3)–Mo(1)–Mo(3)	47.30(7)	O(2)–Mo(3)–N(9)	94.3(1)
O(3)–Mo(1)–O(4)	96.0(1)	O(2)–Mo(3)–S(1)	102.17(7)
O(3)–Mo(1)–O(5)	85.30(9)	O(3)–Mo(3)–Mo(1)	47.60(7)
O(3)–Mo(1)–N(1)	168.2(1)	O(3)–Mo(3)–Mo(2)	93.36(7)
O(3)–Mo(1)–S(1)	103.36(7)	O(3)–Mo(3)–N(5)	85.6(1)
O(4)–Mo(1)–Mo(2)	144.93(7)	O(3)–Mo(3)–N(7)	82.6(1)
O(4)–Mo(1)–Mo(3)	103.20(7)	O(3)–Mo(3)–N(9)	163.4(1)
O(4)–Mo(1)–O(5)	78.92(9)	O(3)–Mo(3)–S(1)	102.46(7)
O(4)–Mo(1)–N(1)	83.9(1)	N(5)–Mo(3)–Mo(1)	93.15(8)
O(4)–Mo(1)–S(1)	88.55(7)	N(5)–Mo(3)–Mo(2)	142.40(7)
O(5)–Mo(1)–Mo(2)	135.78(7)	N(5)–Mo(3)–N(7)	87.4(1)
O(5)–Mo(1)–Mo(3)	132.59(7)	N(5)–Mo(3)–N(9)	82.6(1)
O(5)–Mo(1)–N(1)	83.1(1)	N(5)–Mo(3)–S(1)	87.17(7)
O(5)–Mo(1)–S(1)	165.54(7)	N(7)–Mo(3)–Mo(1)	129.89(8)
N(1)–Mo(1)–Mo(2)	94.21(8)	N(7)–Mo(3)–Mo(2)	129.87(7)
N(1)–Mo(1)–Mo(3)	144.18(8)	N(7)–Mo(3)–N(9)	85.2(1)
N(1)–Mo(1)–S(1)	88.40(8)	N(7)–Mo(3)–S(1)	172.22(8)
S(1)–Mo(1)–Mo(2)	56.38(2)	N(9)–Mo(3)–Mo(1)	144.55(8)
S(1)–Mo(1)–Mo(3)	57.21(2)	N(9)–Mo(3)–Mo(2)	103.16(8)
Mo(1)–Mo(2)–Mo(3)	59.53(1)	N(9)–Mo(3)–S(1)	88.59(8)
O(1)–Mo(2)–Mo(1)	47.49(7)	S(1)–Mo(3)–Mo(1)	55.99(2)

O(1)–Mo(2)–Mo(3)	91.86(7)	S(1)–Mo(3)–Mo(2)	56.31(2)
O(1)–Mo(2)–O(2)	94.05(9)	Mo(1)–O(1)–Mo(2)	85.22(9)
O(1)–Mo(2)–O(7)	96.9(2)	Mo(1)–O(3)–Mo(3)	85.10(9)
O(1)–Mo(2)–O(8)	86.2(1)	Mo(1)–S(1)–Mo(2)	67.87(2)
O(1)–Mo(2)–N(3)	169.6(1)	Mo(1)–S(1)–Mo(3)	66.79(2)
O(1)–Mo(2)–S(1)	102.07(7)	Mo(2)–O(2)–Mo(3)	85.19(9)
O(2)–Mo(2)–Mo(1)	93.83(7)	Mo(2)–S(1)–Mo(3)	66.80(2)
O(2)–Mo(2)–Mo(3)	47.37(7)	C(1)–O(4)–Mo(1)	117.0(2)
O(2)–Mo(2)–O(7)	160.6(1)	C(2)–O(5)–Mo(1)	115.3(2)
O(2)–Mo(2)–O(8)	87.04(9)	C(3)–N(1)–Mo(1)	127.4(3)
O(2)–Mo(2)–N(3)	84.2(1)	C(5)–N(1)–Mo(1)	126.9(3)
O(2)–Mo(2)–S(1)	102.68(7)	C(5A)–N(1)–Mo(1)	129.6(6)
O(7)–Mo(2)–Mo(1)	105.35(8)	C(6)–O(7)–Mo(2)	118.3(2)
O(7)–Mo(2)–Mo(3)	147.53(7)	C(7)–O(8)–Mo(2)	116.5(2)
O(7)–Mo(2)–O(8)	77.79(9)	C(8)–N(3)–Mo(2)	127.9(3)
O(7)–Mo(2)–N(3)	82.2(1)	C(10)–N(3)–Mo(2)	126.2(3)
O(7)–Mo(2)–S(1)	90.67(7)	C(11)–N(5)–Mo(3)	127.8(2)
O(8)–Mo(2)–Mo(1)	133.62(7)	C(13)–N(5)–Mo(3)	126.1(2)
O(8)–Mo(2)–Mo(3)	134.16(7)	C(14)–N(7)–Mo(3)	122.9(2)
O(8)–Mo(2)–N(3)	83.6(1)	C(16)–N(7)–Mo(3)	131.8(2)
O(8)–Mo(2)–S(1)	166.63(7)	C(17)–N(9)–Mo(3)	128.1(2)
N(3)–Mo(2)–Mo(1)	142.73(8)	C(19)–N(9)–Mo(3)	127.7(2)
N(3)–Mo(2)–Mo(3)	94.42(9)		

Table S5. Selected bond distances (Å) and angles (°) for $Na_2[(Mo_3SO_3)(R,S\text{-lact})_3(im)_3]\cdot 10H_2O$ (**2**).

Mo(1)–Mo(2)	2.6158(9)	Mo(2)–O(7)	1.999(7)
Mo(1)–Mo(3)	2.609(1)	Mo(2)–O(8)	2.133(6)
Mo(1)–O(1)	1.941(6)	Mo(2)–N(3)	2.237(8)
Mo(1)–O(3)	1.929(6)	Mo(2)–S(1)	2.366(2)
Mo(1)–O(4)	1.994(6)	Mo(3)–O(2)	1.946(6)
Mo(1)–O(5)	2.135(6)	Mo(3)–O(3)	1.934(6)
Mo(1)–N(1)	2.241(8)	Mo(3)–O(10)	2.003(6)
Mo(1)–S(1)	2.367(2)	Mo(3)–O(11)	2.131(6)
Mo(2)–Mo(3)	2.6114(9)	Mo(3)–N(5)	2.252(8)
Mo(2)–O(1)	1.944(6)	Mo(3)–S(1)	2.373(2)
Mo(2)–O(2)	1.921(6)		
Mo(2)–Mo(1)–Mo(3)	59.98(3)	N(3)–Mo(2)–Mo(3)	95.3(2)
O(1)–Mo(1)–Mo(2)	47.7(2)	N(3)–Mo(2)–S(1)	88.4(2)
O(1)–Mo(1)–Mo(3)	92.8(2)	S(1)–Mo(2)–Mo(1)	56.47(5)
O(1)–Mo(1)–O(4)	160.4(3)	S(1)–Mo(2)–Mo(3)	56.68(5)
O(1)–Mo(1)–O(5)	85.4(3)	Mo(1)–Mo(3)–Mo(2)	60.15(3)
O(1)–Mo(1)–N(1)	84.7(3)	O(2)–Mo(3)–Mo(1)	92.9(2)
O(1)–Mo(1)–S(1)	103.0(2)	O(2)–Mo(3)–Mo(2)	47.1(2)
O(3)–Mo(1)–Mo(2)	93.26(2)	O(2)–Mo(3)–O(3)	94.0(3)
O(3)–Mo(1)–Mo(3)	47.6(2)	O(2)–Mo(3)–O(10)	95.4(3)
O(3)–Mo(1)–O(1)	93.1(3)	O(2)–Mo(3)–O(11)	85.5(3)
O(3)–Mo(1)–O(4)	97.1(3)	O(2)–Mo(3)–N(5)	170.0(3)
O(3)–Mo(1)–O(5)	85.8(3)	O(2)–Mo(3)–S(1)	102.3(2)
O(3)–Mo(1)–N(1)	167.6(3)	O(3)–Mo(3)–Mo(1)	47.5(2)
O(3)–Mo(1)–S(1)	103.0(2)	O(3)–Mo(3)–Mo(2)	93.3(2)
O(4)–Mo(1)–Mo(2)	147.3(2)	O(3)–Mo(3)–O(10)	160.5(3)
O(4)–Mo(1)–Mo(3)	106.5(2)	O(3)–Mo(3)–O(11)	85.8(2)
O(4)–Mo(1)–O(5)	78.8(2)	O(3)–Mo(3)–N(5)	86.2(3)
O(4)–Mo(1)–N(1)	81.7(3)	O(3)–Mo(3)–S(1)	102.7(2)
O(4)–Mo(1)–S(1)	91.0(2)	O(10)–Mo(3)–Mo(1)	148.5(2)
O(5)–Mo(1)–Mo(2)	133.0(2)	O(10)–Mo(3)–Mo(2)	105.6(2)
O(5)–Mo(1)–Mo(3)	133.3(2)	O(10)–Mo(3)–O(11)	78.0(2)
O(5)–Mo(1)–N(1)	81.8(3)	O(10)–Mo(3)–N(5)	81.7(3)
O(5)–Mo(1)–S(1)	167.3(2)	O(10)–Mo(3)–S(1)	92.0(2)
N(1)–Mo(1)–Mo(2)	94.3(2)	O(11)–Mo(3)–Mo(1)	133.0(2)
N(1)–Mo(1)–Mo(3)	144.6(2)	O(11)–Mo(3)–Mo(2)	132.4(2)
N(1)–Mo(1)–S(1)	89.4(2)	O(11)–Mo(3)–N(5)	84.6(3)
S(1)–Mo(1)–Mo(2)	56.44(5)	O(11)–Mo(3)–S(1)	168.0(2)
S(1)–Mo(1)–Mo(3)	56.71(6)	N(5)–Mo(3)–Mo(1)	94.4(2)
Mo(1)–Mo(2)–Mo(3)	59.87(3)	N(5)–Mo(3)–Mo(2)	142.9(2)
O(1)–Mo(2)–Mo(1)	47.6(2)	N(5)–Mo(3)–S(1)	87.4(2)

O(1)–Mo(2)–Mo(3)	92.6(2)	S(1)–Mo(3)–Mo(1)	56.50(5)
O(1)–Mo(2)–O(2)	93.0(3)	S(1)–Mo(3)–Mo(2)	56.44(5)
O(1)–Mo(2)–O(7)	95.8(3)	Mo(1)–O(1)–Mo(2)	84.6(2)
O(1)–Mo(2)–O(8)	86.7(3)	Mo(1)–S(1)–Mo(2)	67.10(6)
O(1)–Mo(2)–N(3)	168.5(3)	Mo(1)–O(3)–Mo(3)	84.9(3)
O(1)–Mo(2)–S(1)	102.9(2)	Mo(1)–S(1)–Mo(3)	66.78(6)
O(2)–Mo(2)–Mo(1)	93.3(2)	Mo(2)–O(2)–Mo(3)	85.0(2)
O(2)–Mo(2)–Mo(3)	47.9(2)	Mo(2)–O(8)–Na(2)	147.0(4)
O(2)–Mo(2)–O(7)	161.5(3)	Mo(2)–S(1)–Mo(3)	66.87(6)
O(2)–Mo(2)–O(8)	86.0(3)	C(1)–O(4)–Mo(1)	116.7(6)
O(2)–Mo(2)–N(3)	86.2(3)	C(2)–O(5)–Mo(1)	114.9(6)
O(2)–Mo(2)–S(1)	103.3(2)	C(4)–N(1)–Mo(1)	125.4(7)
O(7)–Mo(2)–Mo(1)	104.64(2)	C(6)–N(1)–Mo(1)	128.1(7)
O(7)–Mo(2)–Mo(3)	147.33(2)	C(7)–O(7)–Mo(2)	117.9(7)
O(7)–Mo(2)–O(8)	78.3(3)	C(8)–O(8)–Mo(2)	114.9(7)
O(7)–Mo(2)–N(3)	82.0(3)	C(10)–N(3)–Mo(2)	126.0(7)
O(7)–Mo(2)–S(1)	90.7(2)	C(12)–N(3)–Mo(2)	128.5(6)
O(8)–Mo(2)–Mo(1)	134.3(2)	C(13)–O(10)–Mo(3)	116.8(9)
O(8)–Mo(2)–Mo(3)	133.8(2)	C(13A)–O(10)–Mo(3)	115.0(7)
O(8)–Mo(2)–N(3)	81.8(3)	C(14)–O(11)–Mo(3)	116.9(6)
O(8)–Mo(2)–S(1)	166.1(2)	C(16)–N(5)–Mo(3)	124.9(6)
N(3)–Mo(2)–Mo(1)	143.8(2)	C(18)–N(5)–Mo(3)	129.2(7)

Table S6. Selected bond distances (Å) and angles (°) for $[(Mo_6O_{10})(R,S\text{-lact})_2(im)_{10}]\cdot 16H_2O$ (**3**).

Mo(1)–Mo(2a)	2.5034(7)	Mo(2)–O(7a)	2.201(4)
Mo(1)–Mo(3)	2.5550(8)	Mo(2)–N(5)	2.207(5)
Mo(1)–O(1)	2.044(4)	Mo(3)–Mo(2a)	2.5282(8)
Mo(1)–O(2a)	1.948(4)	Mo(3)–O(1)	2.052(4)
Mo(1)–O(4)	2.000(4)	Mo(3)–O(3)	1.915(4)
Mo(1)–O(5)	1.911(4)	Mo(3)–O(4)	1.895(4)
Mo(1)–N(1)	2.237(5)	Mo(3)–O(8)	2.165(4)
Mo(1)–N(3)	2.198(5)	Mo(3)–N(7)	2.202(6)
Mo(2)–Mo(1a)	2.5035(7)	Mo(3)–N(9)	2.186(6)
Mo(2)–Mo(3a)	2.5282(8)	Mo(1a)–O(2)	1.948(4)
Mo(2)–O(1a)	2.045(4)	Mo(2a)–O(1)	2.045(4)
Mo(2)–O(2)	1.908(4)	Mo(2a)–O(3)	2.003(4)
Mo(2)–O(3a)	2.003(4)	Mo(2a)–O(7)	2.201(4)
Mo(2)–O(5)	1.900(4)		
Mo(2a)–Mo(1)–Mo(3)	59.96(2)	O(7a)–Mo(2)–Mo(3a)	85.3(1)
O(1)–Mo(1)–Mo(2a)	52.3(1)	O(7a)–Mo(2)–N(5)	86.6(2)
O(1)–Mo(1)–Mo(3)	51.6(1)	N(5)–Mo(2)–Mo(1a)	136.3(1)
O(1)–Mo(1)–O(4)	96.8(2)	N(5)–Mo(2)–Mo(3a)	133.0(1)
O(1)–Mo(1)–O(5)	90.0(2)	Mo(2a)–Mo(3)–Mo(1)	59.01(2)
O(1)–Mo(1)–O(2a)	101.0(2)	O(1)–Mo(3)–Mo(1)	51.3(1)
O(1)–Mo(1)–N(1)	86.6(2)	O(1)–Mo(3)–Mo(2a)	51.8(1)
O(1)–Mo(1)–N(3)	173.9(2)	O(1)–Mo(3)–O(3)	102.5(2)
O(4)–Mo(1)–Mo(2a)	97.0(1)	O(1)–Mo(3)–O(4)	99.9(2)
O(4)–Mo(1)–Mo(3)	47.3(1)	O(1)–Mo(3)–O(8)	84.5(2)
O(4)–Mo(1)–O(5)	165.0(2)	O(1)–Mo(3)–N(7)	86.3(2)
O(4)–Mo(1)–O(2a)	95.4(2)	O(1)–Mo(3)–N(9)	168.4(2)
O(4)–Mo(1)–N(1)	83.5(2)	O(3)–Mo(3)–Mo(1)	95.1(1)
O(4)–Mo(1)–N(3)	84.0(2)	O(3)–Mo(3)–Mo(2a)	51.4(1)
O(5)–Mo(1)–Mo(2a)	97.8(1)	O(4)–Mo(3)–O(3)	99.7(2)
O(5)–Mo(1)–Mo(3)	141.5(1)	O(3)–Mo(3)–O(8)	84.3(2)
O(5)–Mo(1)–O(2a)	96.6(2)	O(3)–Mo(3)–N(7)	160.4(2)
O(5)–Mo(1)–N(1)	83.5(2)	O(3)–Mo(3)–N(9)	84.9(2)
O(5)–Mo(1)–N(3)	87.9(2)	O(4)–Mo(3)–Mo(1)	50.8(1)
O(2a)–Mo(1)–Mo(2a)	48.8(1)	O(4)–Mo(3)–Mo(2a)	99.0(1)
O(2a)–Mo(1)–Mo(3)	90.7(1)	O(4)–Mo(3)–O(8)	173.2(2)
O(2a)–Mo(1)–N(1)	172.4(2)	O(4)–Mo(3)–N(7)	96.0(2)
O(2a)–Mo(1)–N(3)	85.0(2)	O(4)–Mo(3)–N(9)	87.5(2)
N(1)–Mo(1)–Mo(2a)	138.8(1)	O(8)–Mo(3)–Mo(1)	134.7(1)
N(1)–Mo(1)–Mo(3)	94.0(1)	O(8)–Mo(3)–Mo(2a)	87.8(1)
N(1)–Mo(1)–N(3)	87.4(2)	O(8)–Mo(3)–N(7)	79.0(2)
N(3)–Mo(1)–Mo(2a)	133.8(1)	O(8)–Mo(3)–N(9)	87.4(2)

N(3)–Mo(1)–Mo(3)	130.5(1)	N(7)–Mo(3)–Mo(1)	104.0(2)
Mo(1a)–Mo(2)–Mo(3a)	61.03(2)	N(7)–Mo(3)–Mo(2a)	137.2(2)
O(2)–Mo(2)–Mo(1a)	50.2(1)	N(7)–Mo(3)–N(9)	84.0(2)
O(2)–Mo(2)–Mo(3a)	92.4(1)	N(9)–Mo(3)–Mo(1)	137.8(2)
O(2)–Mo(2)–O(5)	102.6(2)	N(9)–Mo(3)–Mo(2a)	136.2(2)
O(2)–Mo(2)–O(1a)	102.4(2)	Mo(1)–O(5)–Mo(2)	160.4(2)
O(2)–Mo(2)–O(3a)	89.3(2)	Mo(1)–O(1)–Mo(2a)	75.5(2)
O(2)–Mo(2)–O(7a)	167.7(2)	Mo(1)–O(1)–Mo(3)	77.2(2)
O(2)–Mo(2)–N(5)	86.1(2)	Mo(1)–O(4)–Mo(3)	81.9(2)
O(5)–Mo(2)–Mo(1a)	101.2(1)	Mo(1a)–O(2)–Mo(2)	81.0(2)
O(5)–Mo(2)–Mo(3a)	139.7(1)	Mo(2a)–O(1)–Mo(3)	76.2(1)
O(5)–Mo(2)–O(1a)	88.0(2)	Mo(2a)–O(3)–Mo(3)	80.3(2)
O(5)–Mo(2)–O(3a)	164.2(2)	C(2)–O(7)–Mo(2a)	123.7(4)
O(5)–Mo(2)–O(7a)	86.8(2)	C(2)–O(8)–Mo(3)	123.4(4)
O(5)–Mo(2)–N(5)	85.7(2)	C(4)–N(1)–Mo(1)	124.4(4)
O(1a)–Mo(2)–Mo(1a)	52.2(1)	C(6)–N(1)–Mo(1)	130.0(5)
O(1a)–Mo(2)–Mo(3a)	52.0(1)	C(7)–N(3)–Mo(1)	126.3(4)
O(1a)–Mo(2)–O(7a)	85.8(2)	C(9)–N(3)–Mo(1)	128.1(4)
O(1a)–Mo(2)–N(5)	170.4(2)	C(10)–N(5)–Mo(2)	128.5(4)
O(3a)–Mo(2)–Mo(1a)	94.5(1)	C(12)–N(5)–Mo(2)	125.3(5)
O(3a)–Mo(2)–Mo(3a)	48.3(1)	C(13)–N(7)–Mo(3)	126.0(5)
O(3a)–Mo(2)–O(1a)	99.7(2)	C(15)–N(7)–Mo(3)	127.9(5)
O(3a)–Mo(2)–O(7a)	80.2(2)	C(16)–N(9)–Mo(3)	128.0(5)
O(3a)–Mo(2)–N(5)	84.7(2)	C(18)–N(9)–Mo(3)	127.6(5)
O(7a)–Mo(2)–Mo(1a)	136.4(1)		

Symmetry codes: (a) $1 - x$, $1 - y$, $1 - z$;

Table S7. Selected bond distances (Å) and angles (°) for $Na_6[(Mo_2O_4)_3(R,S\text{-mal})_4]\ 5H_2O$ (**4**).

Mo(1)–Mo(1a)	2.557(3)	Mo(2)–O(2)	2.11(1)
Mo(1)–O(1)	2.12(1)	Mo(2)–O(4)	2.07(1)
Mo(1)–O(1b)	2.12(1)	Mo(2)–O(6)	1.67(2)
Mo(1)–O(7)	2.31(2)	Mo(2)–O(7)	1.99(1)
Mo(1)–O(9)	1.71(2)	Mo(2)–O(8)	1.91(1)
Mo(1)–O(10)	1.93(1)	Mo(1a)–O(10)	1.93(1)
Mo(1)–O(10a)	1.93(1)	Mo(2b)–O(7)	1.99(1)
Mo(2)–Mo(2b)	2.597(2)	Mo(2b)–O(8)	1.91(1)
Mo(2)–O(1)	2.20(1)		
O(1)–Mo(1)–O(7)	71.4(4)	O(4)–Mo(2)–O(8)	84.9(5)
O(1)–Mo(1)–O(10a)	90.0(4)	O(6)–Mo(2)–O(7)	106.5(7)
O(1)–Mo(1)–O(1b)	81.1(6)	O(6)–Mo(2)–O(8)	109.5(7)
O(1)–Mo(1)–O(9)	92.7(5)	O(7)–Mo(2)–O(8)	93.2(5)
O(1)–Mo(1)–O(10)	160.2(7)	O(1)–Mo(1)–Mo(1a)	138.4(3)
O(7)–Mo(1)–O(9)	158.7(6)	O(7)–Mo(1)–Mo(1a)	104.7(4)
O(7)–Mo(1)–O(10)	89.0(6)	O(9)–Mo(1)–Mo(1a)	96.6(5)
O(7)–Mo(1)–O(10a)	89.0(6)	O(10)–Mo(1)–Mo(1a)	48.5(3)
O(7)–Mo(1)–O(1b)	71.4(4)	O(10a)–Mo(1)–Mo(1a)	48.5(3)
O(9)–Mo(1)–O(10)	105.4(7)	O(1b)–Mo(1)–Mo(1a)	138.4(3)
O(9)–Mo(1)–O(10a)	105.4(7)	O(1)–Mo(2)–Mo(2b)	92.1(2)
O(9)–Mo(1)–O(1b)	92.7(5)	O(2)–Mo(2)–Mo(2b)	139.1(3)
O(10)–Mo(1)–O(10a)	92.8(6)	O(4)–Mo(2)–Mo(2b)	132.1(3)
O(10)–Mo(1)–O(1b)	90.0(4)	O(6)–Mo(2)–Mo(2b)	102.3(5)
O(10a)–Mo(1)–O(1b)	160.2(7)	O(7)–Mo(2)–Mo(2b)	49.4(3)
O(1)–Mo(2)–O(2)	72.9(5)	O(8)–Mo(2)–Mo(2b)	47.2(4)
O(1)–Mo(2)–O(4)	80.4(5)	Mo(1)–O(10)–Mo(1a)	83.0(5)
O(1)–Mo(2)–O(6)	163.0(5)	Mo(1)–O(1)–Mo(2)	106.0(5)
O(1)–Mo(2)–O(7)	76.2(6)	Mo(1)–O(7)–Mo(2)	106.5(7)
O(1)–Mo(2)–O(8)	86.8(6)	Mo(1)–O(7)–Mo(2b)	106.5(7)
O(2)–Mo(2)–O(4)	83.8(5)	Mo(2)–O(7)–Mo(2b)	81.3(6)
O(2)–Mo(2)–O(6)	90.3(6)	Mo(2)–O(8)–Mo(2b)	85.6(7)
O(2)–Mo(2)–O(7)	89.8(4)	C(1)–O(1)–Mo(1)	118.0(9)
O(2)–Mo(2)–O(8)	158.2(7)	C(1)–O(1)–Mo(2)	111.4(10)
O(4)–Mo(2)–O(6)	96.0(6)	C(2)–O(2)–Mo(2)	118.4(11)
O(4)–Mo(2)–O(7)	156.6(7)	C(4)–O(4)–Mo(2)	137.0(11)

Symmetry codes: (a) $1 - x, 1 - y, z$; (b) $x, 1 - y, z$;

Table S8. Selected bond distances (Å) and angles (°) within the water layer in $Na_2[(Mo_3SO_3)(R,S\text{-lact})_3(im)_3]\cdot 10H_2O$ (**2**).

D–H···A	D–H(Å)	H···A(Å)	D···A(Å)	D–H···A(°)
N_2–H_2 ··O_{7d}	0.88	1.82	2.68(1)	164
N_4–H_4 ··O_{10e}	0.88	1.83	2.69(1)	166
N_6–H_6 ··O_{4b}	0.88	1.87	2.73(1)	166
O_{9W}–H_{9WA} ··O_{2i}	0.82	2.07	2.80(1)	149
O_{9W}–H_{9WB} ··O_{5Wi}	0.84	1.92	2.71(2)	155
O_{8W}–H_{8WA} ··O_{9W}	0.85	2.03	2.70(2)	136
O_{4W}–H_{4WA} ··O_1	0.86	1.92	2.76(1)	162
O_{10W}–H_{10A} ··O_{12}	0.85	2.03	2.77(1)	146
O_{10W}–H_{10B} ··O_{11i}	0.84	2.17	2.89(1)	143
O_{4W}–H_{4WB} ··O_{2W}	0.85	2.23	2.97(2)	146
O_{7W}–H_{7WA} ··O_{6a}	0.86	2.25	3.10(2)	172
O_{5W}–H_{5WA} ··O_{7W}	0.85	2.04	2.87(1)	165
O_{5W}–H_{5WB} ··O_{6W}	0.86	2.05	2.90(2)	166
O_{7W}–H_{7WB} ··O_{9Wg}	0.87	1.95	2.80(2)	165
O_{8W}–H_{8WB} ··O_{10W}	1.02	2.15	2.81(2)	120
O_{6W}–H_{6WA} ··O_{7Wh}	0.98	2.50	3.12(2)	120
O_{6W}–H_{6WB} ··O_{8Wg}	0.94	2.16	3.01(2)	148
O_{3W}–H_{3WA} ··O_{5a}	0.98	1.88	2.83(1)	163
O_{3W}–H_{3WA} ··O_{6a}	0.98	2.43	3.20(1)	135
O_{3W}–H_{3WB} ··O_{1Wa}	1.00	2.05	3.03(1)	165
O_{1W}–H_{1WA} ··O_{8Wc}	0.85	2.43	2.97(2)	122
O_{1W}–H_{1WB} ··O_{3c}	0.85	2.10	2.86(1)	149
O_{2W}–H_{2WA} ··O_{10Wf}	0.86(10)	1.88(10)	2.71(2)	162(10)

Symmetry codes: (a) 2 – *x*, 1 – *y*, 1 – *z*; (b) 1 – *x*, 1 – *y*, -*z*; (c) 2 – *x*, 2 – *y*, 1 – *z*; (d) 2 – *x*, 1 – *y*, -*z*; (e) 1 – *x*, -*y*, -*z*; (f) 1 + *x*, *y*, *z*; (g) *x*, -1 + *y*, *z*; (h) 1 – *x*, -*y*, 1 – *z*; (i) 1 – *x*, 1 – *y*, 1 – *z*.

Table S9. Bond valence calculations for complexes $[(Mo_3SO_3)\ (glyc)_2(im)_5]\cdot im\cdot H_2O$ (**1**), $Na_2[(Mo_3SO_3)(R,S\text{-lact})_3(im)_3]\cdot 10H_2O$ (**2**), $[(Mo_6O_{10})(R,S\text{-lact})_2(im)_{10}]\cdot 16H_2O$ (**3**), and $Na_6[(Mo_2O_4)_3(R,S\text{-mal})_4]\ 5H_2O$ (**4**).

Complexes	Atoms	N	$\sum S_{ij}$	Δ
$[(Mo_3SO_3)\ (glyc)_2(im)_5]\cdot im\cdot H_2O$ (**1**)	Mo(1)	4+	4.062	0.062
	Mo(2)	4+	3.984	0.016
	Mo(3)	4+	3.995	0.005
$Na_2[(Mo_3SO_3)(R,S\text{-lact})_3(im)_3]\cdot 10H_2O$ (**2**)	Mo(1)	4+	3.966	0.034
	Mo(2)	4+	3.979	0.021
	Mo(3)	4+	3.927	0.073
$[(Mo_6O_{10})(R,S\text{-lact})_2(im)_{10}]\cdot 16H_2O$ (**3**)	Mo(1)	4+	4.110	0.110
	Mo(2)	4+	4.014	0.014
	Mo(3)	4+	4.039	0.039
$Na_6[(Mo_2O_4)_3(R,S\text{-mal})_4]\ 5H_2O$ (**4**)	Mo(1)	5+	5.018	0.018
	Mo(2)	5+	5.239	0.239

Table S10. The bond distances of Mo–$O_{\alpha\text{-alkoxy/hydroxy}}$, Mo–$O_{\alpha\text{-carboxy}}$ and C–$O_{\alpha\text{-alkoxy/hydroxy}}$ from FeMo-cofactors of MoFe-proteins in nitrogenases.

Entry	PDB ID	Resolutions	Mo–$O_{\alpha\text{-alkoxy/hydroxy}}$	Distances	Mo–$O_{\alpha\text{-carboxy}}$	Distances	C–$O_{\alpha\text{-alkoxy/hydroxy}}$	Distances
1	5VPW[13]	1.85 Å	[ICS]602:A.MO1–[HCA]601:A.O7	2.119	[ICS]602:A.MO1–[HCA]601:A.O6	2.287	[HCA]601:A.C3–[HCA]601:A.O7	1.438
			[ICS]602:C.MO1–[HCA]601:C.O7	2.147	[ICS]602:C.MO1–[HCA]601:C.O5	2.253	[HCA]601:C.C3–[HCA]601:C.O7	1.450
2	5VQ3[13]	1.72 Å	[ICS]602:C.MO1–[HCA]601:C.O7	2.164	[ICS]602:C.MO1–[HCA]601:C.O5	2.224	[HCA]601:C.C3–[HCA]601:C.O7	1.426
			[ICS]602:A.MO1–[HCA]601:A.O7	2.133	[ICS]602:A.MO1–[HCA]601:A.O6	2.213	[HCA]601:A.C3–[HCA]601:A.O7	1.443
3	5VQ4[13]	2.3 Å	[ICS]502:C.MO1–[HCA]501:C.O7	2.171	[ICS]502:C.MO1–[HCA]501:C.O5	2.162	[HCA]501:C.C3–[HCA]501:C.O7	1.475
			[ICS]502:A.MO1–[HCA]501:A.O7	2.066	[ICS]502:A.MO1–[HCA]501:A.O6	2.240	[HCA]501:A.C3–[HCA]501:A.O7	1.445
4	4WZA[14]	1.9 Å	[ICS]1496:A.MO1–[HCA]1494:A.O7	2.222	[ICS]1496:A.MO1–[HCA]1494:A.O5	1.986	[HCA]1494:A.C3–[HCA]1494:A.O7	1.436
			[ICS]1496:C.MO1–[HCA]1494:C.O7	2.212	[ICS]1496:C.MO1–[HCA]1494:C.O5	1.979	[HCA]1494:C.C3–[HCA]1494:C.O7	1.440
5	5KOH[15]	1.83 Å	[ICS]502:C.MO1–[HCA]501:C.O7	2.143	[ICS]502:C.MO1–[HCA]501:C.O5	2.184	[HCA]501:C.C3–[HCA]501:C.O7	1.415
			[ICS]502:A.MO1–[HCA]501:A.O7	2.117	[ICS]502:A.MO1–[HCA]501:A.O6	2.150	[HCA]501:A.C3–[HCA]501:A.O7	1.441
6	5KOJ[15]	2.59 Å	[ICS]502:C.MO1–[HCA]501:C.O7	1.981	[ICS]502:C.MO1–[HCA]501:C.O5	2.362	[HCA]501:C.C3–[HCA]501:C.O7	1.424
			[ICS]502:A.MO1–	2.182	[ICS]502:A.MO1–	2.247	[HCA]501:A.C3–	1.431

			[HCA]501:A.O7		[HCA]501:A.O5		[HCA]501:A.O7	
7	5BVG[16]	1.6 Å	[ICG]502:C.MO1–[HCA]501:C.O7	2.244	[ICG]502:C.MO1–[HCA]501:C.O5	2.201	[ICG]501:C.C7–[HCA]501:C.O7	1.445
			[ICG]502:A.MO1–[HCA]501:A.O7	2.178	[ICG]502:A.MO1–[HCA]501:A.O6	2.242	[ICG]501:A.C3–[HCA]501:A.O7	1.435
8	5BVH[16]	1.53 Å	[ICH]503:C.MO1–[HCA]501:C.O7	2.241	[ICH]503:C.MO1–[HCA]501:C.O5	2.249	[HCA]501:C.C3–[HCA]501:C.O7	1.432
			[ICH]503:A.MO1–[HCA]501:A.O7	2.258	[ICH]503:A.MO1–[HCA]501:A.O6	2.202	[HCA]501:A.C3–[HCA]501:A.O7	1.444
9	4XPI[17]	1.97 Å	[ICS]502:C.MO1–[HCA]501:C.O7	2.303	[ICS]502:C.MO1–[HCA]501:C.O5	2.029	[HCA]501:C.C3–[HCA]501:C.O7	1.441
			[ICS]502:A.MO1–[HCA]501:A.O7	2.151	[ICS]502:A.MO1–[HCA]501:A.O6	2.144	[HCA]501:A.C3–[HCA]501:A.O7	1.440
10	5CX1[18]	1.75 Å	[ICS]502:E.MO1–[HCA]501:E.O7	2.355	[ICS]502:E.MO1–[HCA]501:E.O6	2.648	[HCA]501:E.C3–[HCA]501:E.O7	1.417
			[ICS]502:G.MO1–[HCA]501:G.O7	2.650	[ICS]502:G.MO1–[HCA]501:G.O5	2.291	[HCA]501:G.C3–[HCA]501:G.O7	1.428
			[ICS]502:M.MO1–[HCA]501:M.O7	2.648	[ICS]502:M.MO1–[HCA]501:M.O5	2.277	[HCA]501:M.C3–[HCA]501:M.O7	1.428
			[ICS]502:O.MO1–[HCA]501:O.O7	2.662	[ICS]502:O.MO1–[HCA]501:O.O6	2.310	[HCA]501:O.C3–[HCA]501:O.O7	1.424
			[ICS]502:C.MO1–[HCA]501:C.O7	2.676	[ICS]502:C.MO1–[HCA]501:C.O5	2.354	[HCA]501:C.C3–[HCA]501:C.O7	1.445
			[ICS]502:A.MO1–[HCA]501:A.O7	2.668	[ICS]502:A.MO1–[HCA]501:A.O6	2.357	[HCA]501:A.C3–[HCA]501:A.O7	1.405
			[ICS]502:I.MO1–	2.376	[ICS]502:I.MO1–	2.652	[HCA]501:I.C3–	1.449

			[HCA]501:I.O7			[HCA]501:I.O5		[HCA]501:I.O7	
			[ICS]502:K.MO1–[HCA]501:K.O7	2.364		[ICS]502:K.MO1–[HCA]501:K.O6	2.666	[HCA]501:K.C3–[HCA]501:K.O7	1.433
11	4WN9[19]	1.9 Å	[ICS]602:C.MO1–[HCA]601:C.O7	2.047		[ICS]602:C.MO1–[HCA]601:C.O5	2.231	[HCA]601:C.C3–[HCA]601:C.O7	1.446
			[ICS]602:A.MO1–[HCA]601:A.O7	2.158		[ICS]602:A.MO1–[HCA]601:A.O5	2.143	[HCA]601:A.C3–[HCA]601:A.O7	1.426
12	4WNA[19]	2.0 Å	[ICS]502:C.MO1–[HCA]501:C.O7	2.054		[ICS]502:C.MO1–[HCA]501:C.O5	2.275	[HCA]501:C.C3–[HCA]501:C.O7	1.427
			[ICS]502:A.MO1–[HCA]501:A.O7	2.110		[ICS]502:A.MO1–[HCA]501:A.O5	2.159	[HCA]501:A.C3–[HCA]501:A.O7	1.430
13	4WZB[20]	2.3 Å	[ICS]1496:A.MO1–[HCA]1494:A.O7	2.504		[ICS]1496:A.MO1–[HCA]1494:A.O5	1.914	[HCA]1494:A.C3–[HCA]1494:A.O7	1.438
			[ICS]1496:C.MO1–[HCA]1494:C.O7	2.540		[ICS]1496:C.MO1–[HCA]1494:C.O5	1.912	[HCA]1494:C.C3–[HCA]1494:C.O7	1.434
14	4WES[21]	1.08 Å	[ICS]602:C.MO1–[HCA]601:C.O7	2.174		[ICS]602:C.MO1–[HCA]601:C.O6	2.223	[HCA]601:C.C3–[HCA]601:C.O7	1.440
			[ICS]602:A.MO1–[HCA]601:A.O7	2.201		[ICS]602:A.MO1–[HCA]601:A.O5	2.220	[HCA]601:A.C3–[HCA]601:A.O7	1.421
15	4TKU[22]	1.43 Å	[ICS]502:C.MO1–[HCA]501:C.O7	2.227		[ICS]502:C.MO1–[HCA]501:C.O5	2.189	[HCA]501:C.C3–[HCA]501:C.O7	1.444
			[ICS]502:A.MO1–[HCA]501:A.O7	2.215		[ICS]502:A.MO1–[HCA]501:A.O5	2.204	[HCA]501:A.C3–[HCA]501:A.O7	1.439
16	4TKV[22]	1.5 Å	[ICE]502:C.MO1–[HCA]501:C.O7	2.195		[ICE]502:C.MO1–[HCA501:C.O5	2.195	[HCA]501:C.C3–[HCA]501:C.O7	1.442
			[ICE]502:A.MO1–	2.217		[ICE]502:A.MO1–	2.166	[HCA]501:A.C3–	1.436

			[HCA]501:A.O7		[HCA]501:A.O6		[HCA]501:A.O7	
17	4ND8[23]	2.0 Å	[ICS]502:C.MO1–[HCA]501:C.O7	2.283	[ICS]502:C.MO1–[HCA]501:C.O5	2.424	HCA]501:C.C3–[HCA]501:C.O7	1.447
			[ICS]502:A.MO1–[HCA]501:A.O7	2.205	[ICS]502:A.MO1–[HCA]501:A.O5	2.427	[HCA]501:A.C3–[HCA]501:A.O7	1.434
18	3U7Q[24]	1.0 Å	[ICS]7496:C.MO1–[HCA]7494:C.O7	2.178	[ICS]7496:C.MO1–[HCA]7494:C.O5	2.212	[HCA]7494:C.C3–[HCA]7494:C.O7	1.447
			[ICS]6496:A.MO1–[HCA]6494:A.O7	2.164	[ICS]6496:A.MO1–[HCA]6494:A.O5	2.192	[HCA]6494:A.C3–[HCA]6494:A.O7	1.442
19	3K1A[25]	2.23 Å	[CFN]7496:C.MO1–[HCA]494:C.O7	2.250	[CFN]7496:C.MO1–[HCA]494:C.O5	2.171	[HCA]494:C.C3–[HCA]494:C.O7	1.454
			[CFN]6496:A.MO1–[HCA]494:A.O7	2.160	[CFN]6496:A.MO1–[HCA]494:A.O5	2.169	[HCA]494:A.C3–[HCA]494:A.O7	1.447
20	2AFH[20]	2.1 Å	[CFN]2496:A.MO1–[HCA]2494:A.O7	2.242	[CFN]2496:A.MO1–[HCA]2494:A.O5	2.334	[HCA]2494:A.C3–[HCA]2494:A.O7	1.494
			[CFN]3496:C.MO1–[HCA]3494:C.O7	2.123	[CFN]3496:C.MO1–[HCA]3494:C.O5	2.331	[HCA]3494:C.C3–[HCA]3494:C.O7	1.488
21	2AFI[20]	3.1 Å	[CFN]496:C.MO1–[HCA]494:C.O7	2.165	[CFN]496:C.MO1–[HCA]494:C.O5	2.163	[HCA]494:C.C3–[HCA]494:C.O7	1.479
			[CFN]496:A.MO1–[HCA]494:A.O7	2.213	[CFN]496:A.MO1–[HCA]494:A.O5	2.124	[HCA]494:A.C3–[HCA]494:A.O7	1.508
			[CFN]496:K.MO1–[HCA]494:K.O7	2.199	[CFN]496:K.MO1–[HCA]494:K.O5	2.152	[HCA]494:K.C3–[HCA]494:K.O7	1.510
			[CFN]496:I.MO1–[HCA]494:I.O7	2.221	[CFN]496:I.MO1–[HCA]494:I.O5	2.124	[HCA]494:I.C3–[HCA]494:I.O7	1.473
22	1M1Y[26]	3.2 Å	[CFM]9496:K.MO1	2.057	[CFM]9496:K.MO1	2.285	[HCA]9494:K.C3–	1.518

			–[HCA]9494:K.O7		–[HCA]9494:K.O5		[HCA]9494:K.O7	
			[CFM]7496:C.MO1–	1.947	[CFM]7496:C.MO1–	2.193	[HCA]7494:C.C3–	1.525
			[HCA]7494:C.O7		[HCA]7494:C.O5		[HCA]7494:C.O7	
23	1M34[26]	2.3 Å	[CFM]4296:K.MO1	2.993	[CFM]4296:K.MO1	3.156	[HCA]4294:K.C3–	1.490
			–[HCA]4294:K.O7		–[HCA]4294:K.O5		[HCA]4294:K.O7	
			[CFM]4096:I.MO1–	3.535	[CFM]4096:I.MO1–	3.091	[HCA]4094:I.C3–	1.418
			[HCA]4094:I.O7		[HCA]4094:I.O5		[HCA]4094:I.O7	
			[CFM]2096:A.MO1	2.954	[CFM]2096:A.MO1	3.044	[HCA]2094:A.C3–	1.421
			–[HCA]2094:A.O7		–[HCA]2094:A.O5		[HCA]2094:A.O7	
			[CFM]2296:C.MO1–	2.939	[CFM]2296:C.MO1–	2.869	[HCA]2094:C.C3–	1.438
			[HCA]2294:C.O7		[HCA]2294:C.O5		[HCA]2294:C.O7	
24	1FP4[27]	2.5 Å	[CFM]496:A.MO1–	2.179	[CFM]496:A.MO1–	2.205	[HCA]494:A.C3–	1.427
			[HCA]494:A.O7		[HCA]494:A.O5		[HCA]494:A.O7	
			[CFM]497:C.MO1–	2.193	[CFM]497:C.MO1–	2.203	[HCA]495:C.C3–	1.429
			[HCA]495:C.O7		[HCA]495:C.O5		[HCA]495:C.O7	
25	1M1N[28]	1.16 Å	[CFN]7496:C.MO1–	2.199	[CFN]7496:C.MO1–	2.181	[HCA]7494:C.C3–	1.461
			[HCA]7494:C.O7		[HCA]7494:C.O5		[HCA]7494:C.O7	
			[CFN]6496:A.MO1–	2.184	[CFN]6496:A.MO1–	2.180	[HCA]6494:A.C3–	1.414
			[HCA]6494:A.O7		[HCA]6494:A.O5		[HCA]6494:A.O7	
			[CFN]8496:E.MO1–	2.213	[CFN]8496:E.MO1–	2.162	[HCA]8494:E.C3–	1.446
			[HCA]8494:E.O7		[HCA]8494:E.O5		[HCA]8494:E.O7	
			[CFN]9496:G.MO1–	2.194	[CFN]9496:G.MO1–	2.194	[HCA]9494:G.C3–	1.464
			[HCA]9494:G.O7		[HCA]9494:G.O5		[HCA]9494:G.O7	
26	1H1L[29]	1.9 Å	[CFM]1480:A.MO1	2.250	[CFM]1480:A.MO1	2.313	[CIT]1479:A.C3–	1.447
			–[CIT]1479:A.O7		–[CIT]1479:A.O5		[HCA]1479:A.O7	
			[CFM]1480:C.MO1–	2.254	[CFM]1480:C.MO1–	2.270	[CIT]1479:C.C3–	1.429

			[CIT]1479:C.O7		[CIT]1479:C.O5		[CIT]1479:C.O7	
27	1G20[30]	2.2 Å	[CFM]3496:C.MO1–[HCA]3494:C.O7	2.153	[CFM]3496:C.MO1–[HCA]3494:C.O5	2.194	[HCA]3494:C.C3–[HCA]3494:C.O7	1.451
			[CFM]1496:A.MO1–[HCA]1494:A.O7	2.218	[CFM]1496:A.MO1–[HCA]1494:A.O5	2.163	[HCA]1494:A.C3–[HCA]1494:A.O7	1.459
28	1G21[30]	3.0 Å	[CFM]3496:C.MO1–[HCA]3494:C.O7	2.177	[CFM]3496:C.MO1–[HCA]3494:C.O5	2.222	[HCA]3494:C.C3–[HCA]3494:C.O7	1.417
			[CFM]1496:A.MO1–[HCA]1494:A.O7	2.208	[CFM]1496:A.MO1–[HCA]1494:A.O5	2.270	[HCA]1494:A.C3–[HCA]1494:A.O7	1.433
29	1QGU[31]	1.6 Å	[CFM]503:A.MO1–[HCA]501:A.O7	2.351	[CFM]503:A.MO1–[HCA]501:A.O5	2.293	[HCA]501:A.C3–[HCA]501:A.O7	1.526
			[CFM]503:C.MO1–[HCA]501:C.O7	2.351	[CFM]503:C.MO1–[HCA]501:C.O5	2.277	[HCA]501:C.C3–[HCA]501:C.O7	1.514
30	1QH1[31]	1.6 Å	[CFM]503:A.MO1–[HCA]501:A.O7	2.371	[CFM]503:A.MO1–[HCA]501:A.O5	2.310	[HCA]501:A.C3–[HCA]501:A.O7	1.500
			[CFM]503:C.MO1–[HCA]501:C.O7	2.327	[CFM]503:C.MO1–[HCA]501:C.O5	2.271	[HCA]501:C.C3–[HCA]501:C.O7	1.512
31	1QH8[31]	1.6 Å	[CFM]503:A.MO1–[HCA]501:A.O7	2.364	[CFM]503:A.MO1–[HCA]501:A.O5	2.321	[HCA]501:A.C3–[HCA]501:A.O7	1.506
			[CFM]503:C.MO1–[HCA]501:C.O7	2.337	[CFM]503:C.MO1–[HCA]501:C.O5	2.286	[HCA]501:C.C3–[HCA]501:C.O7	1.526
32	1N2C[32]	3.0 Å	[CFM]496:C.MO1–[HCA]494:C.O7	2.168	[CFM]496:C.MO1–[HCA]494:C.O5	2.208	[HCA]494:C.C3–[HCA]494:C.O7	1.446
			[CFM]496:A.MO1–[HCA]494:A.O7	2.185	[CFM]496:A.MO1–[HCA]494:A.O5	2.173	[HCA]494:A.C3–[HCA]494:A.O7	1.425
33	2MIN[33]	2.03 Å	[CFM]496:C.MO1–	2.077	[CFM]496:C.MO1–	2.105	[HCA]494:C.C3–	1.471

			[HCA]494:C.O7		[HCA]494:C.O5		[HCA]494:C.O7	
			[CFM]496:A.MO1–[HCA]494:A.O7	2.093	[CFM]496:A.MO1–[HCA]494:A.O5	2.081	[HCA]494:A.C3–[HCA]494:A.O7	1.451
34	3MIN[33]	2.03 Å	[CFM]496:C.MO1–[HCA]494:C.O7	2.050	[CFM]496:C.MO1–[HCA]494:C.O5	2.066	[HCA]494:C.C3–[HCA]494:C.O7	1.443
			[CFM]496:A.MO1–[HCA]494:A.O7	1.995	[CFM]496:A.MO1–[HCA]494:A.O5	2.037	[HCA]494:A.C3–[HCA]494:A.O7	1.423
35	1MIO[34]	3.0 Å	[CFM]496:D.MO1–[HCA]494:D.O7	2.188	[CFM]496:D.MO1–[HCA]494:D.O5	2.182	[HCA]494:D.C3–[HCA]494:D.O7	1.428
			[CFM]496:B.MO1–[HCA]494:B.O7	2.193	[CFM]496:B.MO1–[HCA]494:B.O5	2.196	[HCA]494:B.C3–[HCA]494:B.O7	1.432
36	6BBL[35]	1.68 Å	[ICS]503:C.MO1–[HCA]502:C.O7	2.238	[ICS]503:C.MO1–[HCA]502:C.O5	2.241	[HCA]502:C.C3–[HCA]502:C.O7	1.430
			[ICS]504:A.MO1–[HCA]503:A.O7	2.237	[ICS]504:A.MO1–[HCA]503:A.O5	2.274	HCA]503:A.C3–[HCA]503:A.O7	1.433
	Average			**2.272**		**2.263**		**1.449**

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