Supporting materials

Gas adsorption of mixed valence trinuclear oxo-thiomolybdenum glycolates

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Figure and Table Options

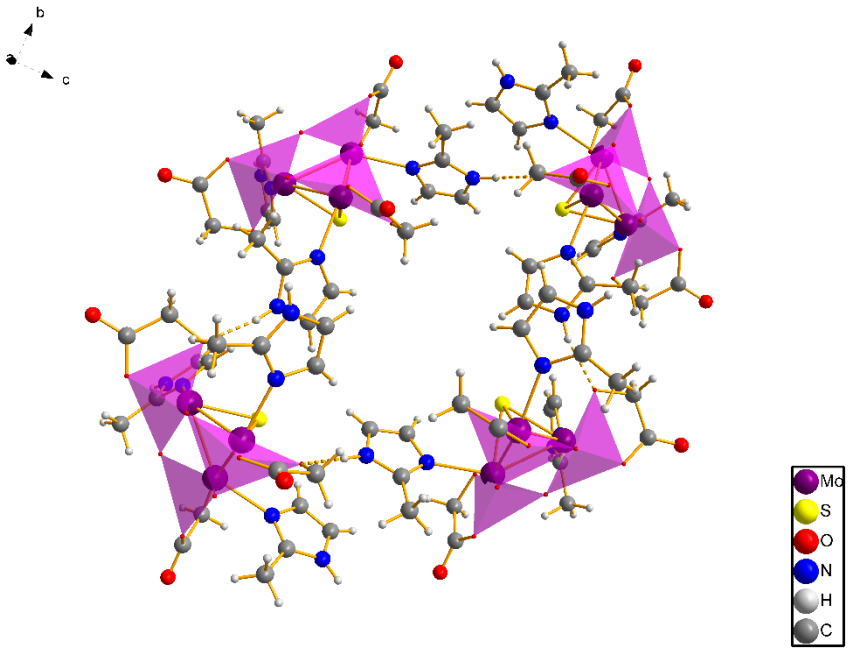

Figure S1. 3D layered diagram of the molecular structure in $Na_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(glyc)_3(2\text{-}mim)_3]\cdot 1.5H_2O$ (**1**), sodium ions are omitted for clarity.

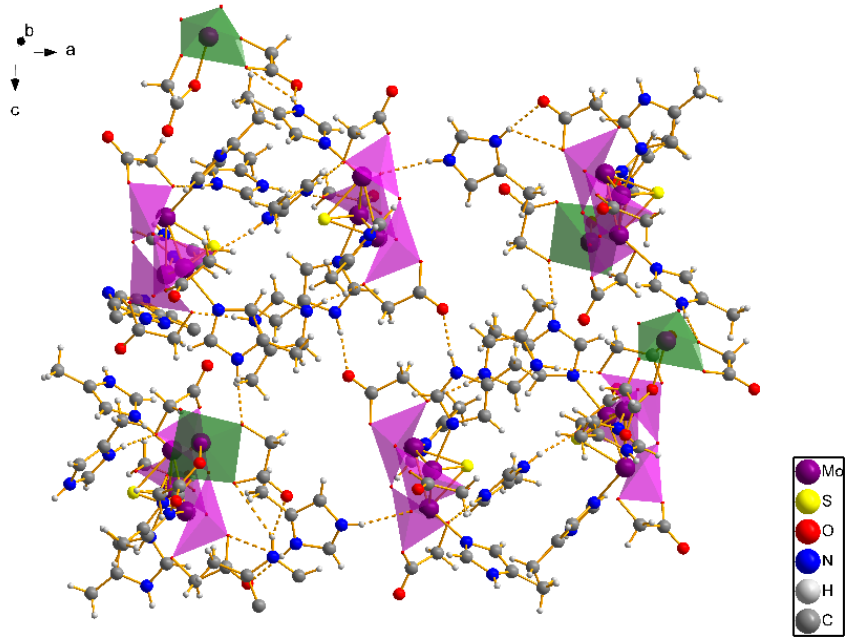

Figure S2. 3D layered diagram of the molecular structure in $(4\text{-}Hmim)_6[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(glyc)_3(4\text{-}mim)_3]_2[MoO_2(glyc)_2]$ (**2**), some protonated 4-methylimidazoles are omitted for clarity.

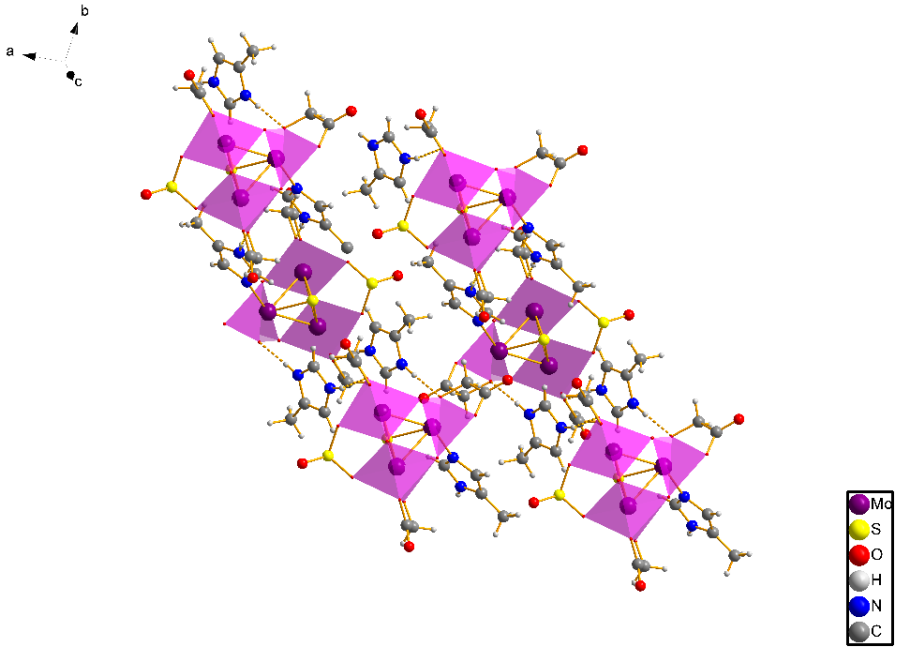

Figure S3. 3D layered diagram of the molecular structure in $Na_3(4\text{-}Hmim)[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(SO_3)(glyc)_3(4\text{-}mim)]\cdot 8H_2O$ (**3**), water molecules and sodium ions are omitted for clarity.

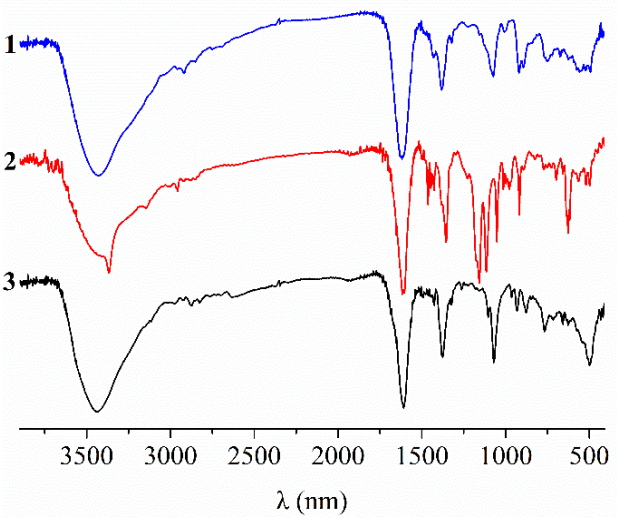

Figure S4. IR spectra of $Na_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(glyc)_3(2\text{-}mim)_3]\cdot 1.5H_2O$ (**1**), $(4\text{-}Hmim)_6[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(glyc)_3(4\text{-}mim)_3]_2[MoO_2(glyc)_2]$ (**2**), and $Na_3(4\text{-}Hmim)[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(SO_3)(glyc)_3(4\text{-}mim)]\cdot 8H_2O$ (**3**).

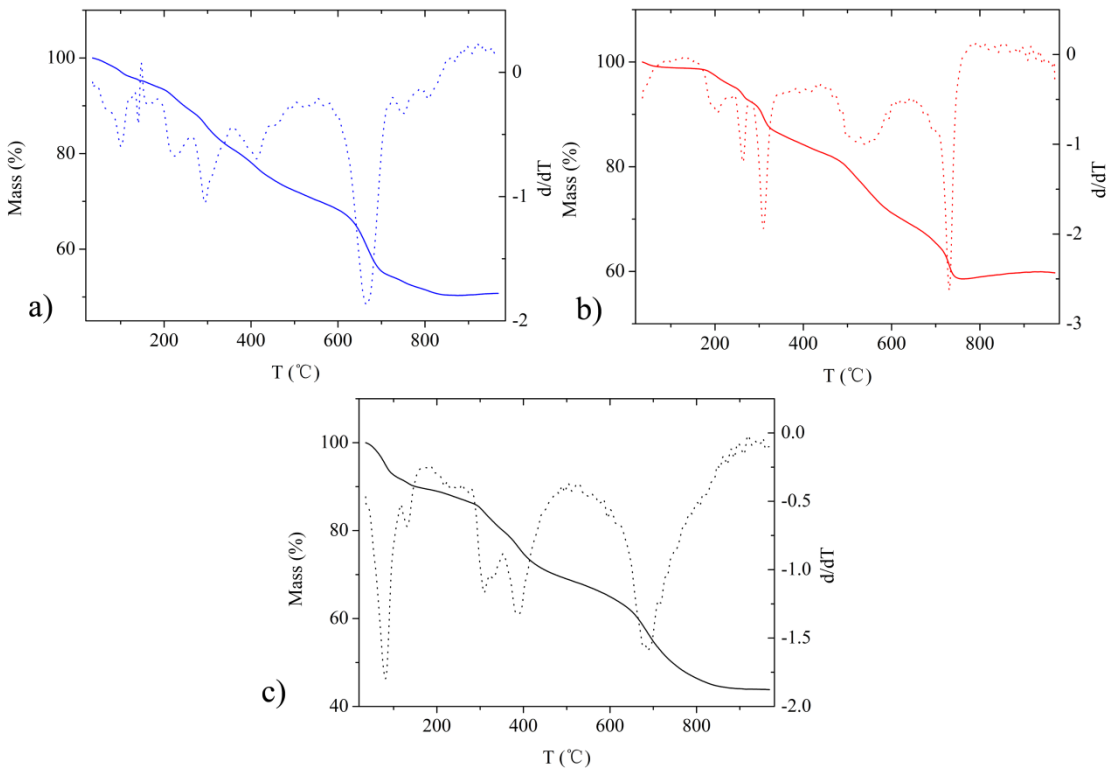

Figure S5. TGA curves of polycrystalline sample $Na_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(glyc)_3(2\text{-}mim)_3]\cdot 1.5H_2O$ (**1**, a), $(4\text{-}Hmim)_6[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(glyc)_3(4\text{-}mim)_3]_2[MoO_2(glyc)_2]$ (**2**, b), and $Na_3(4\text{-}Hmim)[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(SO_3)(glyc)_3(4\text{-}mim)]\cdot 8H_2O$ (**3**, c).

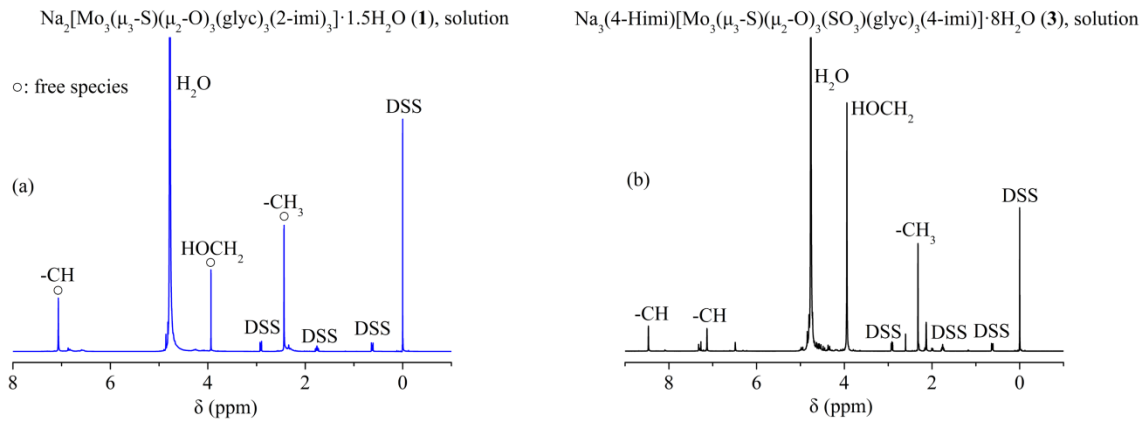

Figure S6. Solution ^1H NMR spectra of $Na_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(glyc)_3(2\text{-}mim)_3]\cdot 1.5H_2O$ (**1**, a) and $Na_3(4\text{-}Hmim)[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(SO_3)(glyc)_3(4\text{-}mim)]\cdot 8H_2O$ (**3**, b).

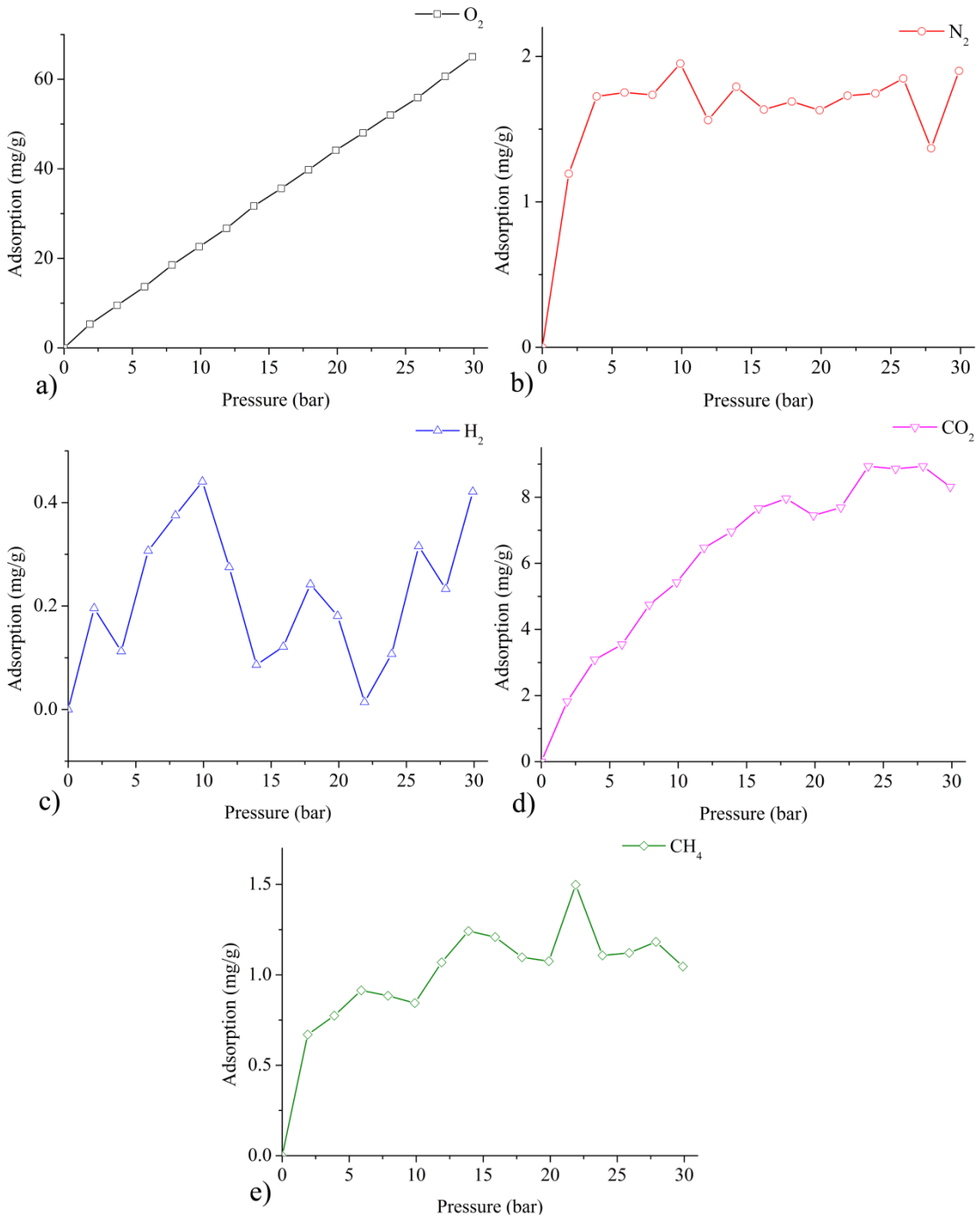

Figure S7. Gases adsorption isotherms (O_2, a; N_2, b; H_2, c; CO_2, d; CH_4, e) of $(4\text{-Hmim})_6[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(glyc)_3(4\text{-}mim)_3]_2[MoO_2(glyc)_2]$ (**2**) at 298 K in different pressures.

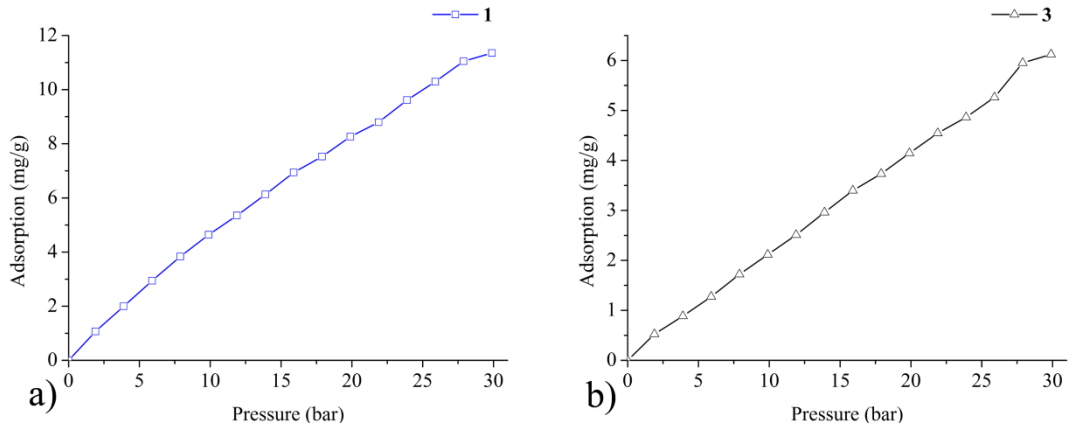

Figure S8. O_2 adsorption isotherms of $Na_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(glyc)_3(2\text{-}mim)_3]\cdot 1.5H_2O$ (**1**, a) and $Na_3(4\text{-}Hmim)[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(SO_3)(glyc)_3(4\text{-}mim)]\cdot 8H_2O$ (**3**, b) at 298 K.

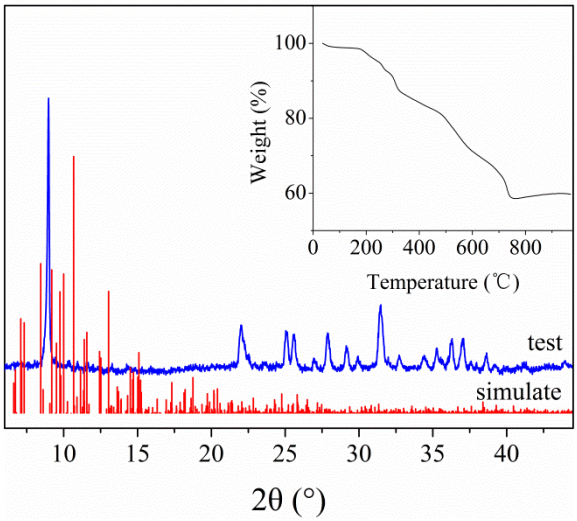

Figure S9. XRD patterns (from bottom to top) for **2** (simulated), **2** (experimental). Inset: TGA curves for **2**.

Table S1. Crystallographic data and structural refinements for complexes $Na_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(glyc)_3(2\text{-}mim)_3]\cdot 1.5H_2O$ (**1**) $(4\text{-}Hmim)_6[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(glyc)_3(4\text{-}mim)_3]_2[MoO_2(glyc)_2]$ (**2**) and $Na_3(4\text{-}Hmim)[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(SO_3)(glyc)_3(4\text{-}mim)]\cdot 8H_2O$ (**3**).

Identification codes	**1**	**2**	**3**
Empirical formula	$C_{18}H_{24}Mo_3N_6Na_2O_{13.5}S$	$C_{64}H_{87}Mo_7N_{24}O_{32}S_2$	$C_{14}H_{35}Mo_3N_4Na_3O_{23}S_2$
Formula weight	906.18	2440.27	1048.37
Temperature/K	100.0(1)	100.0	100.0(1)
Crystal system	cubic	monoclinic	triclinic
Space group	*P a-3*	*I 2/a*	*P* $\bar{1}$
a/Å	30.72520(1)	35.5920(2)	10.85260(1)
b/Å	30.72520(1)	20.9894(2)	11.18150(1)
c/Å	30.72520(1)	36.5014(2)	15.71790(1)
α/°	90	90	108.6890(1)
β/°	90	95.8250(1)	105.9850(1)
γ/°	90	90	98.5290(1)
Volume/Å^3	29005.8(3)	27127.7(3)	1677.28(3)
Z	32	8	2
d_{calc}g/cm^3	1.660	1.195	2.076
μ/mm^{-1}	9.689	5.952	11.462
F(000)	14270.0	9768.0	1044.0
Crystal size/mm^3	0.10 × 0.08 × 0.05	0.02 × 0.03 × 0.05	0.40 × 0.30 × 0.05
Radiation	CuKα (λ = 1.54178)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2θ range for data collection/ °	4.982 to 134.096	4.862 to 136.502	8.646 to 148.044
Index ranges	-33 ≤ h ≤ 33, -22 ≤ k ≤ 29, -11 ≤ l ≤ 36	-42 ≤ h ≤ 42, -20 ≤ k ≤ 25, -42 ≤ l ≤ 43	-13 ≤ h ≤ 13, -13 ≤ k ≤ 12, -19 ≤ l ≤ 19
Reflections collected	31361	86001	19041
Independent reflections	8581 [R_{int} = 0.0441, R_{sigma} = 0.0394]	24733 [R_{int} = 0.0424, R_{sigma} = 0.0392]	6403 [R_{int} = 0.0306, R_{sigma} = 0.0279]
Data/restraints/parameters	8581/79/569	24733/501/1255	6403/103/518
Goodness–of–fit on F^2	1.098	1.087	1.078
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0706, wR_2 = 0.1894	R_1 = 0.0559, wR_2 = 0.1700	R_1 = 0.0288, wR_2 = 0.0755

Final *R* indexes [all data]	R_1 = 0.0790, wR_2 = 0.1961	R_1 = 0.0679, wR_2 = 0.1854	R_1 = 0.0323, wR_2 = 0.0776
Largest diff. peak/hole / e Å^{-3}	3.90/-1.24	1.53/-1.35	1.59/-0.91

Table S2. Selected hydrogen bond distances (Å) and angles (°) in $Na_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(glyc)_3(2\text{-}mim)_3]\cdot 1.5H_2O$ (**1**).

D–H ··A	D–H(Å)	H ··A(Å)	D ··A(Å)	D–H ··A(°)
N2–H2 ··O16a	0.88	1.95	2.800(9)	161
N4–H4 ··O14b	0.88	1.89	2.763(8)	170
N6–H6 ··O11c	0.88	1.93	2.789(8)	165
N8–H8 ··O12c	0.88	1.99	2.848(8)	165

Symmetry codes: (a) ½ + *x*, *y*, ½ – *z*; (b) 1 – *z*, 1 – *x*, 1 – *y*; (c) 3/2 – *y*, ½ + *z*, -1 + *x*.

Table S3. Selected hydrogen bond distances (Å) and angles (°) in $(4\text{-}Hmim)_6[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(glyc)_3(4\text{-}mim)_3]_2[MoO_2(glyc)_2]$ (**2**).

D–H ··A	D–H(Å)	H ··A(Å)	D ··A(Å)	D–H ··A(°)
N2–H2 ··O32a	0.88	1.88	2.757(6)	176
N4–H4 ··O29b	0.88	1.86	2.734(6)	173
N8–H8 ··O31	0.88	1.92	2.754(8)	157
N10–H10 ··O22c	0.88	1.85	2.726(7)	173
N13–H13 ··O3	0.88	1.72	2.592(5)	172
N14–H14A ··O15	0.88	1.72	2.602(5)	177
N15–H15A ··O7	0.88	1.72	2.601(6)	174
N16–H16 ··O19	0.88	1.74	2.617(6)	177
N17–H17 ··O11	0.88	1.76	2.637(6)	178
N18–H18A ··O23	0.88	1.75	2.624(6)	175
N19–H19 ··O6d	0.88	1.97	2.852(1)	177
N20–H20 ··O16	0.88	2.14	3.006(8)	167
N22–H22 ··O21	0.88	2.08	2.903(1)	157
N22–H22 ··O24	0.88	2.55	3.172(1)	128'
N22–H22C ··O21	0.88	2.12	2.903(1)	148

Symmetry codes: (a) *x*, ½ – *y*, ½ + *z*; (b) 1 – *x*, 1 – *y*, 1 – *z*; (c) 3/2 – *x*, ½ – *y*, 3/2 – *z*; (d) ½ + *x*, 1 – *y*, *z*.

Table S4. Selected hydrogen bond distances (Å) and angles (°) in $Na_3(4\text{-}Hmim)[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(SO_3)(glyc)_3(4\text{-}mim)]\cdot 8H_2O$ (**3**).

D–H ··A	D–H(Å)	H ··A(Å)	D ··A(Å)	D–H ··A
O1w–H1wA ··O9	0.85	1.93	2.769(4)	170
N2–H2 ··O10e	0.88(6)	1.84(6)	2.714(4)	173(5)
O1w–H1wB ··O6wd	0.85	2.12	2.935(4)	161
N3–H3 ··O7	0.86	1.79	2.651(4)	176
O7w–H7wA ··O14a	0.9	2.51	2.837(5)	102
N4–H4 ··O4j	0.86	1.81	2.654(4)	167
O7w–H7wB ··O14a	0.9	2.25	2.837(5)	122
O8w–H8wA ··O2	0.84(7)	2.47(6)	2.991(3)	121(5)
O8w–H8wA ··O5	0.84(7)	2.50(7)	3.326(4)	167(5)'
O8w–H8wA ··O13	0.84(7)	2.60(6)	3.151(4)	125(5)''
O8w–H8wB ··O3b	0.78(7)	2.31(7)	3.090(4)	174(7)
O5w–H5wA ··O6g	0.84(7)	1.96(7)	2.790(4)	170(5)
O5w–H5wB ··O9i	0.89(7)	2.02(7)	2.867(3)	159(6)
O4w–H4wA ··O8f	0.73(5)	2.18(5)	2.910(4)	177(7)
O4w–H4wB ··O13	0.81(6)	2.15(7)	2.945(4)	164(7)
O6w–H6wA ··O3wa	0.84(7)	1.98(7)	2.792(5)	162(6)
O6w–H6wB ··O15a	0.87(7)	1.94(7)	2.745(4)	153(6)
O3w–H3wA ··O6c	0.79(8)	2.00(7)	2.727(4)	153(8)
O3w–H3wB ··O3f	0.81(6)	1.91(5)	2.725(4)	178(7)
O2w–H2wA ··O1b	1.05(9)	1.90(1)	2.685(4)	129(7)
O2w–H2wB ··O12h	0.80(7)	1.97(6)	2.765(4)	173(7)

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

Table S5. Selected bond distances (Å) and angles (°) for $Na_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(glyc)_3(2\text{-}mim)_3]\cdot 1.5H_2O$ (**1**).

Mo1–S1	2.365(2)	Mo3–O11	2.011(5)
Mo1–O3	1.931(6)	Mo3–O2	1.913(5)
Mo1–O1	1.926(6)	Mo3–O10	2.187(6)
Mo1–O4	2.001(6)	Mo3–O3	1.930(6)
Mo1–O5	2.160(6)	Mo3–N5	2.250(6)
Mo1–N1	2.256(7)	S2–Mo4a	2.366(2)
Mo2–Mo1	2.617(9)	S2–Mo4b	2.366(2)
Mo2–S1	2.365(2)	O13–Mo4a	1.933(5)
Mo2–O8	1.991(6)	Mo4–Mo4a	2.616(1)
Mo2–O2	1.927(5)	Mo4–Mo4b	2.616(1)
Mo2–O7	2.171(6)	Mo4–S2	2.366(2)
Mo2–O1	1.923(6)	Mo4–O15	2.173(5)
Mo2–N3	2.257(6)	Mo4–O14	2.011(5)
Mo3–Mo2	2.613(8)	Mo4–O13b	1.933(5)
Mo3–Mo1	2.622(9)	Mo4–O13	1.915(5)
Mo3–S1	2.362(2)	Mo4–N7	2.263(6)
O3–Mo1–O5	85.9(3)	N5–Mo3–Mo1	142.84(2)
O3–Mo1–N1	88.3(2)	N5–Mo3–S1	87.49(2)
O1–Mo1–Mo3	91.99(2)	Mo2–Mo3–Mo1	60.00(2)
O1–Mo1–Mo2	47.13(2)	S1–Mo3–Mo2	56.51(5)
O1–Mo1–S1	102.51(2)	S1–Mo3–Mo1	56.36(5)
O1–Mo1–O3	92.7(2)	O11–Mo3–Mo2	147.92(2)
O1–Mo1–O4	95.6(2)	O11–Mo3–Mo1	105.74(2)
O1–Mo1–O5	84.8(3)	O11–Mo3–S1	91.45(2)
O1–Mo1–N1	169.6(3)	O11–Mo3–O10	78.1(2)
O4–Mo1–Mo3	148.14(2)	O11–Mo3–N5	81.2(2)
O4–Mo1–Mo2	104.76(2)	O2–Mo3–Mo2	47.34(2)
O4–Mo1–S1	91.88(2)	O2–Mo3–Mo1	92.59(2)
O4–Mo1–O5	78.7(3)	O2–Mo3–S1	102.72(2)
O4–Mo1–N1	80.7(2)	O2–Mo3–O11	161.1(2)
O5–Mo1–Mo3	132.88(2)	O2–Mo3–O10	86.1(2)
O5–Mo1–Mo2	131.82(2)	Mo4a–Mo4–Mo4b	60
O5–Mo1–S1	168.7(2)	S2–Mo4–Mo4b	56.43(4)
O5–Mo1–N1	85.0(3)	S2–Mo4–Mo4a	56.43(4)
N1–Mo1–Mo3	96.21(2)	O15–Mo4–Mo4b	132.84(1)
Mo2–Mo1–Mo3	59.83(2)	O15–Mo4–Mo4a	132.92(1)
S1–Mo1–Mo3	56.26(5)	O15–Mo4–S2	167.88(2)
S1–Mo1–Mo2	56.42(5)	O15–Mo4–N7	83.70(2)
O3–Mo1–Mo3	47.21(2)	O14–Mo4–Mo4b	104.46(2)
O3–Mo1–Mo2	92.79(2)	O14–Mo4–Mo4a	148.47(1)

O3–Mo1–S1	102.16(2)	O14–Mo4–S2	92.03(2)
O3–Mo1–O4	161.8(2)	O14–Mo4–O15	78.3(2)
N1–Mo1–Mo2	143.2(2)	O14–Mo4–N7	81.1(2)
N1–Mo1–S1	87.4(2)	O13b–Mo4–Mo4a	92.20(1)
Mo3–Mo2–Mo1	60.18(2)	O13–Mo4–Mo4a	47.45(2)
S1–Mo2–Mo3	56.39(5)	O13b–Mo4–Mo4b	46.89(2)
S1–Mo2–Mo1	56.40(5)	O13–Mo4–Mo4b	92.60(2)
O8–Mo2–Mo3	105.51(2)	O13–Mo4–S2	102.74(2)
O8–Mo2–Mo1	147.62(2)	O13b–Mo4–S2	102.19(2)
O8–Mo2–S1	91.26(2)	O13–Mo4–O15	85.6(2)
O8–Mo2–O7	78.4(2)	O13b–Mo4–O15	86.0(2)
O8–Mo2–N3	81.8(2)	O13–Mo4–O14	161.8(2)
O2–Mo2–Mo3	46.91(2)	O13b–Mo4–O14	94.8(2)
O2–Mo2–Mo1	92.42(2)	O13–Mo4–O13b	92.4(3)
O2–Mo2–S1	102.17(2)	O13b–Mo4–N7	169.5(2)
O2–Mo2–O8	96.7(2)	O13–Mo4–N7	88.9(2)
O2–Mo2–O7	85.4(2)	N7–Mo4–Mo4b	143.46(2)
O2–Mo2–N3	169.5(2)	N7–Mo4–Mo4a	96.33(2)
O7–Mo2–Mo3	132.29(2)	N7–Mo4–S2	87.64(2)
O7–Mo2–Mo1	133.46(2)	C2–O5–Mo1	114.1(7)
O7–Mo2–S1	167.88(2)	C3–N1–Mo1	124.5(6)
O7–Mo2–N3	84.0(2)	Mo3–S1–Mo1	67.38(6)
O1–Mo2–Mo3	92.32(2)	Mo3–O3–Mo1	85.5(2)
O1–Mo2–Mo1	47.21(2)	Mo2–O1–Mo1	85.7(2)
O1–Mo2–S1	102.57(2)	C1–O4–Mo1	116.4(7)
O1–Mo2–O8	161.6(2)	C5–N1–Mo1	129.1(6)
O1–Mo2–O2	92.2(2)	C11–N3–Mo2	129.3(6)
O1–Mo2–O7	86.4(2)	C9–N3–Mo2	122.9(5)
O1–Mo2–N3	86.5(2)	Mo3–S1–Mo2	67.10(6)
N3–Mo2–Mo3	143.56(2)	Mo1–S1–Mo2	67.18(6)
N3–Mo2–Mo1	94.38(2)	C7–O8–Mo2	117.8(5)
N3–Mo2–S1	88.31(2)	Mo3–O2–Mo2	85.8(2)
O2–Mo3–O3	93.2(2)	C8–O7–Mo2	113.3(6)
O2–Mo3–N5	86.9(2)	C15–N5–Mo3	127.5(5)
O10–Mo3–Mo2	133.34(1)	C17–N5–Mo3	129.4(5)
O10–Mo3–Mo1	133.18(2)	C14–O11–Mo3	116.5(5)
O10–Mo3–S1	167.36(2)	C13–O10–Mo3	114.0(5)
O10–Mo3–N5	83.9(2)	C21–N7–Mo4	124.6(5)
O3–Mo3–Mo2	92.96(2)	C23–N7–Mo4	129.4(5)
O3–Mo3–Mo1	47.26(2)	Mo4a–S2–Mo4	67.13(8)
O3–Mo3–S1	102.31(2)	Mo4b–S2–Mo4	67.13(8)
O3–Mo3–O11	95.9(2)	Mo4b–S2–Mo4a	67.13(8)
O3–Mo3–O10	86.0(2)	C20–O15–Mo4	114.0(5)
O3–Mo3–N5	169.9(2)	C19–O14–Mo4	116.5(4)

N5–Mo3–Mo2	94.52(2)	Mo4–O13–Mo4a	85.7(2)

Symmetry codes: (a) 3/2 – *y*, 1 – *z*, -1/2 + *x*; (b) 1/2 + *z*, 3/2 – *x*, 1 – *y*.

Table S6. Selected bond distances (Å) and angles (°) for $(4\text{-Hmim})_6[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(glyc)_3(4\text{-mim})_3]_2[MoO_2(glyc)_2]$ (**2**).

Mo1–Mo2	2.619(5)	Mo4–O13	2.141(4)
Mo1–Mo3	2.612(6)	Mo4–O15	2.003(4)
Mo1–S1	2.381(1)	Mo4–O16	1.919(4)
Mo1–O1	2.125(3)	Mo4–O24	1.940(4)
Mo1–O3	2.011(3)	Mo4–N7	2.237(5)
Mo1–O4	1.937(3)	Mo5–Mo6	2.605(7)
Mo1–O12	1.903(4)	Mo5–S2	2.375(1)
Mo1–N1	2.224(4)	Mo5–O16	1.940(4)
Mo2–Mo3	2.607(6)	Mo5–O17	2.157(5)
Mo2–O4	1.918(3)	Mo5–O19	2.014(4)
Mo2–O5	2.145(4)	Mo5–O20	1.915(4)
Mo2–O7	2.016(3)	Mo5–N9	2.225(5)
Mo2–O8	1.926(4)	Mo6–S2	2.369(1)
Mo2–N3	2.236(4)	Mo6–O20	1.937(4)
Mo2–S1	2.367(1)	Mo6–O21	2.140(4)
Mo3–S1	2.374(1)	Mo6–O23	2.017(4)
Mo3–O8	1.924(3)	Mo6–O24	1.924(4)
Mo3–O9	2.120(4)	Mo6–N11	2.222(6)
Mo3–O11	2.008(3)	Mo7–O25	1.705(5)
Mo3–O12	1.937(4)	Mo7–O26	1.712(5)
Mo3–N5	2.239(5)	Mo7–O27	2.223(5)
Mo4–Mo5	2.613(7)	Mo7–O29	1.963(4)
Mo4–Mo6	2.610(5)	Mo7–O30	2.175(5)
Mo4–S2	2.373(1)	Mo7–O32	1.955(5)
O1–Mo1–Mo3	130.57(1)	O4–Mo1–O3	93.22(2)
O1–Mo1–S1	169.68(1)	O4–Mo1–N1	169.32(2)
O1–Mo1–N1	83.79(2)	Mo3–Mo1–Mo2	59.781(2)
O3–Mo1–Mo2	106.34(9)	S1–Mo1–Mo2	56.26(3)
O3–Mo1–Mo3	151.12(9)	S1–Mo1–Mo3	56.54(3)
O3–Mo1–S1	94.58(9)	O1–Mo1–Mo2	132.51(1)
O3–Mo1–O1	78.00(1)	O12–Mo1–Mo2	92.98(1)
O3–Mo1–N1	81.48(1)	O12–Mo1–Mo3	47.69(1)
O4–Mo1–Mo2	46.92(1)	O12–Mo1–S1	102.99(1)
O4–Mo1–Mo3	93.02(1)	O12–Mo1–O1	83.04(2)
O4–Mo1–S1	101.67(1)	O12–Mo1–O3	159.07(1)
O4–Mo1–O1	86.04(1)	O12–Mo1–O4	94.26(2)
O12–Mo1–N1	87.76(2)	O9–Mo3–S1	168.28(1)
N1–Mo1–Mo2	143.54(1)	O9–Mo3–N5	82.41(2)
N1–Mo1–Mo3	96.08(1)	O11–Mo3–Mo1	104.32(1)
N1–Mo1–S1	88.05(1)	O11–Mo3–Mo2	148.59(1)

O4–Mo2–Mo1	47.50(1)	O11–Mo3–S1	92.09(1)
O4–Mo2–Mo3	93.61(1)	O11–Mo3–O9	78.59(2)
O4–Mo2–S1	102.76(1)	O11–Mo3–N5	82.84(2)
O4–Mo2–O5	84.75(2)	O12–Mo3–Mo1	46.61(1)
O4–Mo2–O7	160.31(2)	O12–Mo3–Mo2	92.57(1)
O4–Mo2–O8	93.48(2)	O12–Mo3–S1	102.20(1)
O4–Mo2–N3	87.16(2)	O12–Mo3–O9	85.70(2)
O5–Mo2–Mo1	132.10(1)	O12–Mo3–O11	94.11(2)
O5–Mo2–Mo3	133.38(1)	O12–Mo3–N5	168.08(2)
O5–Mo2–S1	167.62(1)	N5–Mo3–Mo1	145.31(1)
O5–Mo2–N3	83.91(2)	N5–Mo3–Mo2	96.02(1)
N3–Mo2–S1	86.61(1)	N5–Mo3–S1	89.45(1)
Mo3–Mo2–Mo1	59.98(2)	Mo6–Mo4–Mo5	59.83(2)
S1–Mo2–Mo1	56.78(3)	S2–Mo4–Mo5	56.65(4)
S1–Mo2–Mo3	56.77(3)	S2–Mo4–Mo6	56.53(3)
O7–Mo2–Mo1	149.85(1)	O13–Mo4–Mo5	133.20(1)
O7–Mo2–Mo3	104.94(1)	O13–Mo4–Mo6	132.32(1)
O7–Mo2–S1	93.08(1)	O13–Mo4–S2	167.85(1)
O7–Mo2–O5	77.75(2)	O13–Mo4–N7	84.15(2)
O7–Mo2–N3	82.10(2)	O15–Mo4–Mo5	148.23(1)
O8–Mo2–Mo1	92.29(1)	O15–Mo4–Mo6	107.58(9)
O8–Mo2–Mo3	47.36(1)	O15–Mo4–S2	91.74(1)
O8–Mo2–S1	103.01(1)	O15–Mo4–O13	77.74(2)
O8–Mo2–O5	86.14(2)	O15–Mo4–N7	81.91(2)
O8–Mo2–O7	94.29(2)	O16–Mo4–Mo5	47.73(1)
O8–Mo2–N3	169.94(1)	O16–Mo4–Mo6	92.48(1)
N3–Mo2–Mo1	95.52(1)	O16–Mo4–S2	103.27(1)
N3–Mo2–Mo3	142.65(1)	O16–Mo4–O13	85.60(2)
Mo2–Mo3–Mo1	60.24(2)	O16–Mo4–O15	159.47(2)
S1–Mo3–Mo1	56.81(3)	O16–Mo4–O24	93.19(2)
S1–Mo3–Mo2	56.51(3)	O16–Mo4–N7	84.55(2)
O8–Mo3–Mo1	92.54(1)	O24–Mo4–Mo5	93.13(1)
O8–Mo3–Mo2	47.42(1)	O24–Mo4–Mo6	47.26(1)
O8–Mo3–S1	102.81(1)	O24–Mo4–S2	102.34(1)
O8–Mo3–O9	85.25(2)	O24–Mo4–O13	85.22(2)
O8–Mo3–O11	161.90(2)	O24–Mo4–O15	97.25(2)
O8–Mo3–O12	92.74(2)	O24–Mo4–N7	169.26(2)
O8–Mo3–N5	87.03(2)	N7–Mo4–Mo5	93.09(1)
O9–Mo3–Mo1	132.16(1)	N7–Mo4–Mo6	143.19(1)
O9–Mo3–Mo2	132.56(1)	N7–Mo4–S2	88.39(1)
Mo6–Mo5–Mo4	60.04(2)	Mo5–Mo6–Mo4	60.13(2)
S2–Mo5–Mo4	56.59(4)	S2–Mo6–Mo4	56.69(3)
S2–Mo5–Mo6	56.59(3)	S2–Mo6–Mo5	56.81(4)
O16–Mo5–Mo4	47.05(1)	O20–Mo6–Mo4	92.85(1)

O16–Mo5–Mo6	92.16(1)	O20–Mo6–Mo5	47.10(1)
O16–Mo5–S2	102.54(1)	O20–Mo6–S2	102.63(1)
O16–Mo5–O17	85.6(2)	O20–Mo6–O21	84.45(2)
O16–Mo5–O19	96.06(2)	O20–Mo6–O23	94.44(2)
O16–Mo5–N9	170.12(2)	O20–Mo6–N11	167.58(2)
O17–Mo5–Mo4	132.62(2)	O21–Mo6–Mo4	132.66(1)
O17–Mo5–Mo6	133.52(2)	O21–Mo6–Mo5	131.41(1)
O17–Mo5–S2	167.41(2)	O21–Mo6–S2	168.59(1)
O17–Mo5–N9	84.5(2)	O21–Mo6–N11	83.14(2)
O19–Mo5–Mo4	105.39(1)	O23–Mo6–Mo4	149.18(1)
O19–Mo5–Mo6	148.48(1)	O23–Mo6–Mo5	105.20(1)
O19–Mo5–S2	91.90(1)	O23–Mo6–S2	92.50(1)
O19–Mo5–O17	77.56(2)	O23–Mo6–O21	77.90(2)
O19–Mo5–N9	82.16(2)	O23–Mo6–N11	82.74(2)
O20–Mo5–Mo4	93.30(1)	O24–Mo6–Mo4	47.77(1)
O20–Mo5–Mo6	47.82(1)	O24–Mo6–Mo5	93.75(1)
O20–Mo5–S2	103.11(1)	O24–Mo6–S2	102.98(1)
O20–Mo5–O16	92.71(2)	O24–Mo6–O20	94.20(2)
O20–Mo5–O17	85.9(2)	O24–Mo6–O21	85.20(2)
O20–Mo5–O19	160.54(2)	O24–Mo6–O23	160.15(2)
O20–Mo5–N9	86.23(2)	O24–Mo6–N11	85.00(2)
N9–Mo5–Mo4	142.80(1)	N11–Mo6–Mo4	95.72(1)
N9–Mo5–Mo6	94.38(1)	N11–Mo6–Mo5	145.29(1)
N9–Mo5–S2	87.26(1)	N11–Mo6–S2	89.60(1)
O25–Mo7–O26	105.1(3)	Mo4–S2–Mo5	66.76(4)
O25–Mo7–O27	161.8(2)	Mo6–S2–Mo4	66.78(4)
O25–Mo7–O29	92.0(2)	Mo6–S2–Mo5	66.60(4)
O25–Mo7–O30	88.7(3)	C19–O13–Mo4	115.7(4)
O25–Mo7–O32	103.8(2)	C20–O15–Mo4	117.4(3)
O26–Mo7–O27	90.5(2)	Mo4–O16–Mo5	85.22(2)
O26–Mo7–O29	103.1(2)	C21–O17–Mo5	115.9(4)
O26–Mo7–O30	163.2(2)	C22–O19–Mo5	117.9(4)
O26–Mo7–O32	91.4(2)	Mo5–O20–Mo6	85.08(1)
O29–Mo7–O27	75.0(2)	C23–O21–Mo6	116.4(4)
O29–Mo7–O30	85.6(2)	C24–O23–Mo6	117.2(3)
O30–Mo7–O27	77.8(2)	Mo6–O24–Mo4	84.97(2)
O32–Mo7–O27	84.8(2)	C25–N7–Mo4	127.5(4)
O32–Mo7–O29	155.05(2)	C28–N7–Mo4	126.6(4)
O32–Mo7–O30	75.75(2)	C33–N11–Mo6	128.7(5)
C29–N9–Mo5	128.5(4)	C36–N11–Mo6	126.7(4)
C32–N9–Mo5	127.1(4)	C11–N3–Mo2	127.7(4)
Mo2–S1–Mo1	66.96(3)	C14–N3–Mo2	126.6(3)
Mo2–S1–Mo3	66.72(3)	C15–N5–Mo3	128.3(4)
Mo3–S1–Mo1	66.64(3)	C18–N5–Mo3	125.5(5)

C1–O1–Mo1	116.3(3)	C49–O27–Mo7	115.3(5)
C2–O3–Mo1	117.4(3)	C50–O29–Mo7	122.2(5)
Mo2–O4–Mo1	85.58(1)	C51–O30–Mo7	116.4(4)
C3–O5–Mo2	115.5(4)	C52–O32–Mo7	121.6(4)
C4–O7–Mo2	117.1(4)	Mo1–O12–Mo3	85.70(1)
Mo3–O8–Mo2	85.22(1)	C7–N1–Mo1	128.9(3)
C5–O9–Mo3	115.5(4)	C10–N1–Mo1	126.0(4)
C6–O11–Mo3	117.3(3)		

Table S7. Selected bond distances (Å) and angles (°) for $Na_3(4\text{-Hmim})[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(SO_3)(glyc)_3(4\text{-mim})]\cdot 8H_2O$ (**3**).

Mo1–O5	2.148(2)	Mo2–O3	1.916(2)
Mo1–O4	2.028(2)	Mo2–O1	1.944(2)
Mo1–O1	1.927(2)	Mo3–Mo2	2.6107(3)
Mo1–S1	2.3682(8)	Mo3–Mo1	2.5901(3)
Mo1–O2	1.921(2)	Mo3–O3	1.949(2)
Mo1–O13	2.146(2)	Mo3–O14	2.130(2)
Mo2–Mo1	2.6094(3)	Mo3–S1	2.3713(7)
Mo2–O8	2.146(2)	Mo3–O2	1.941(2)
Mo2–O7	2.027(2)	Mo3–O11	2.140(2)
Mo2–N1	2.216(3)	Mo3–O10	1.994(2)
Mo2–S1	2.3605(7)		
Mo3–Mo1–Mo2	60.278(9)	O8–Mo2–Mo1	131.51(6)
S1–Mo1–Mo2	56.369(2)	O8–Mo2–N1	84.93(9)
O5–Mo1–Mo2	133.63(6)	O3–Mo2–Mo1	92.42(6)
O2–Mo1–Mo3	48.22(6)	O3–Mo2–O8	85.08(8)
O2–Mo1–S1	104.81(6)	O3–Mo2–O1	94.39(9)
O1–Mo1–O4	160.66(9)	O7–Mo2–Mo3	148.18(6)
O2–Mo1–O1	90.42(9)	O7–Mo2–S1	91.48(6)
O4–Mo1–Mo2	108.79(6)	O7–Mo2–N1	84.41(9)
O4–Mo1–O5	78.85(8)	O1–Mo2–Mo1	47.35(6)
O13–Mo1–Mo3	88.86(6)	O1–Mo2–O8	84.49(8)
O13–Mo1–S1	89.86(6)	O1–Mo2–N1	169.41(9)
O1–Mo1–Mo3	94.91(6)	N1–Mo2–Mo1	143.18(7)
O1–Mo1–S1	102.38(7)	S1–Mo2–Mo3	56.710(2)
O1–Mo1–O4	98.73(9)	O8–Mo2–Mo3	132.94(6)
S1–Mo1–Mo3	56.932(2)	O8–Mo2–S1	168.48(6)
O5–Mo1–Mo3	133.05(6)	O3–Mo2–Mo3	48.05(6)
O5–Mo1–S1	166.95(6)	O3–Mo2–S1	103.61(6)
O2–Mo1–Mo2	90.00(6)	O3–Mo2–O7	161.16(9)
O2–Mo1–O5	84.87(8)	O3–Mo2–N1	84.83(9)
O2–Mo1–O13	83.04(9)	O7–Mo2–Mo1	105.42(6)
O4–Mo1–Mo3	146.24(6)	O7–Mo2–O8	78.62(8)
O4–Mo1–S1	89.91(6)	O1–Mo2–Mo3	93.86(6)
O4–Mo1–O13	84.55(8)	O1–Mo2–S1	102.13(6)
O13–Mo1–Mo2	142.49(6)	O1–Mo2–O7	93.37(9)
O13–Mo1–O5	82.56(8)	N1–Mo2–Mo3	93.44(7)
O1–Mo1–Mo2	47.88(6)	N1–Mo2–S1	88.29(7)
O1–Mo1–O5	86.02(9)	Mo1–Mo3–Mo2	60.229(9)
O1–Mo1–O13	167.29(9)	S1–Mo3–Mo1	56.812(2)
Mo1–Mo2–Mo3	59.494(8)	O2–Mo3–Mo1	47.54(6)

S1–Mo2–Mo1	56.643(2)	O2–Mo3–O3	87.59(9)
O2–Mo3–O14	82.72(9)	O2–Mo3–O10	162.84(9)
O3–Mo3–Mo2	46.96(6)	O3–Mo3–Mo1	92.23(6)
O3–Mo3–S1	102.15(6)	O3–Mo3–O11	88.25(9)
O3–Mo3–O14	166.74(9)	O3–Mo3–O10	96.73(9)
O11–Mo3–Mo2	135.12(6)	O11–Mo3–Mo1	132.57(6)
O11–Mo3–S1	166.27(6)	O14–Mo3–Mo2	141.44(6)
O14–Mo3–Mo1	87.90(6)	O14–Mo3–S1	89.01(6)
O14–Mo3–O11	81.95(8)	O10–Mo3–Mo2	105.60(6)
O10–Mo3–Mo1	148.11(6)	O10–Mo3–S1	91.34(6)
O10–Mo3–O11	78.42(9)	O10–Mo3–O14	90.06(9)
S1–Mo3–Mo2	56.318(2)	Mo(2)–S(1)–Mo(1)	66.988(2)
O2–Mo3–Mo2	89.51(6)	Mo(2)–S(1)–Mo(3)	66.973(2)
O2–Mo3–S1	104.02(6)	Mo(1)–S(1)–Mo(3)	66.26(2)
O2–Mo3–O11	85.14(9)		

Table S8. Bond valence calculations for complexes $Na_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(glyc)_3(2\text{-}mim)_3]\cdot 1.5H_2O$ (**1**), $(4\text{-}Hmim)_6[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(glyc)_3(4\text{-}mim)_3]_2[MoO_2(glyc)_2]$ (**2**) and $Na_3(4\text{-}Hmim)[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(SO_3)(glyc)_3(4\text{-}mim)]\cdot 8H_2O$ (**3**).

Complexes	Atoms	N	$\sum S_{ij}$	Δ
$Na_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(glyc)_3(2\text{-}mim)_3]\cdot 1.5H_2O$ (**1**)	Mo1	4+	4.258	0.258
	Mo2	4+	4.277	0.277
	Mo3	4+	4.254	0.254
	Mo(1)	4+	4.351	0.351
	Mo(2)	4+	4.303	0.303
	Mo(3)	4+	4.309	0.309
	Mo(4)	4+	4.292	0.292
	Mo(5)	4+	4.270	0.270
	Mo(6)	4+	4.289	0.289
$(4\text{-}Hmim)_6[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(glyc)_3(4\text{-}mim)_3]_2[MoO_2(glyc)_2]$ (**2**)	Mo(7)	6+	6.110	0.110
$Na_3(4\text{-}Hmim)[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(SO_3)(glyc)_3(4\text{-}mim)]\cdot 8H_2O$ (**3**)	Mo(1)	4+	4.170	0.170
	Mo(2)	4+	4.288	0.288
	Mo(3)	4+	4.163	0.163

Table S9. Spectral data of solution ^{13}C NMR (in ppm) for **1** and **3**.

Compounds	**C**O_2	4-mim/2-mim	**C**O	**C**H_3
1, coordinated	188.76	149.57, 132.23, 117.32	74.65	15.38
1, free	182.58	148.05, 122.92	63.95	14.47
3, coordinated	188.98, 186.61	139.11, 129.63, 120.95,127.23	74.74, 76.64	13.28
3, free	182.59	135.30, 132.42, 118.15	63.93	11.66

Table S10. Detail calibrated adsorption data of O_2, N_2, H_2, CO_2 and CH_4 for **2**.

Gases	O_2		N_2		H_2		CO_2		CH_4	
Temperature (^oC)	Pressure (bar)	Adsorption (mg/g)	Pressure (bar)	Adsorption (mg/g)	Pressure (bar)	Adsorption (mg/g)	Pressure (bar)	Adsorption (mg/g)	Pressure (bar)	Adsorption (mg/g)
25.0	0	0	0	0	0	0	0	0	0	0
	1.900	5.3274	1.899	1.1934	1.920	0.1958	1.890	1.8236	1.902	0.6695
	3.890	9.5173	3.895	1.7251	3.920	0.1122	3.900	3.0817	3.890	0.7740
	5.900	13.6805	5.900	1.7525	5.910	0.3068	5.890	3.5461	5.899	0.9137
	7.900	18.5052	7.896	1.7355	7.930	0.3756	7.895	4.7465	7.897	0.8843
	9.893	22.5883	9.900	1.9507	9.918	0.4407	9.894	5.4248	9.897	0.8440
	11.897	26.6993	11.893	1.5618	11.907	0.2751	11.898	6.4687	11.900	1.0686
	13.898	31.6996	13.910	1.7920	13.910	0.0862	13.895	6.9580	13.901	1.2420
	15.900	35.6294	15.900	1.6350	15.901	0.1214	15.896	7.6606	15.894	1.2088
	17.897	39.7812	17.897	1.6894	17.901	0.2420	17.900	7.9582	17.896	1.0969
	19.895	44.1305	19.895	1.6304	19.911	0.1810	19.893	7.4471	19.903	1.0753
	21.892	48.0227	21.897	1.7300	21.905	0.0142	21.891	7.6880	21.900	1.4980
	23.892	52.0245	23.895	1.7461	23.909	0.1072	23.897	8.9351	23.899	1.1072
	25.895	55.8889	25.895	1.8486	25.906	0.3155	25.893	8.8609	25.896	1.1213
	27.895	60.6231	27.893	1.3684	27.909	0.2330	27.895	8.9342	27.894	1.1825
	29.896	65.0280	29.897	1.9002	29.908	0.4212	29.890	8.3145	29.899	1.0461

Table S11. Detail calibrated adsorption data of O_2 for $Na_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(glyc)_3(2\text{-}mim)_3]\cdot 1.5H_2O$ (**1**), $(4\text{-}Hmim)_6[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(glyc)_3(4\text{-}mim)_3]_2[MoO_2(glyc)_2]$ (**2**), and $Na_3(4\text{-}Hmim)[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(SO_3)(glyc)_3(4\text{-}mim)]\cdot 8H_2O$ (**3**).

Complex	**1**		**2**		**3**	
Temperature (^oC)	Pressure (bar)	Adsorption (mg/g)	Pressure (bar)	Adsorption (mg/g)	Pressure (bar)	Adsorption (mg/g)
25.0	0	0	0	0	0	0
	1.897	1.06703	1.900	5.32744	1.893	0.52376
	3.890	1.99518	3.890	9.51730	3.900	0.88519
	5.897	2.94001	5.900	13.68047	5.896	1.27374
	7.892	3.83354	7.900	18.50517	7.896	1.72067
	9.895	4.64041	9.893	22.58826	9.894	2.11544
	11.892	5.35088	11.897	26.69927	11.897	2.50985
	13.895	6.12772	13.898	31.69961	13.893	2.95951
	15.893	6.93873	15.900	35.62943	15.897	3.39739
	17.894	7.52869	17.897	39.78122	17.894	3.73236
	19.893	8.26412	19.895	44.13047	19.894	4.1449
	21.895	8.79601	21.892	48.02274	21.895	4.54462
	23.894	9.61463	23.892	52.02454	23.895	4.86355
	25.895	10.29478	25.895	55.88886	25.897	5.26156
	27.893	11.04979	27.895	60.62314	27.895	5.95019
	29.893	11.35223	29.896	65.02800	29.893	6.12324