Supporting materials

Molybdenum imidazole citrate and bipyridine homocitrate in different oxidation states – Balance between coordinated α-hydroxy and α-alkoxy groups

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Figure and Table Options

Figure S18. ^{13}C NMR spectrum of $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**) after three months.

Figure S19. ^{1}H NMR spectrum of $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**) after three months.

Figure S20. ^{13}C NMR spectrum of $(Et_4N)[Mo^{VI}O_2Cl(H_2cit)]\cdot H_2O$ (**4**) after three months.

Figure S21. ^{1}H NMR spectrum of $(Et_4N)[Mo^{VI}O_2Cl(H_2cit)]\cdot H_2O$ (**4**) after three months.

Figure S22. XPS spectrum of $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**).

Figure S23. Plots of the experimental temperature dependence of χ_M^{-1} and $\chi_M T$ for $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**).

Figure S24. Plots of the experimental temperature dependence of χ_M^{-1} and $\chi_M T$ for *trans*-$[(Mo^{V}O)_2O(H_2homocit)_2(bpy)_2]\cdot 4H_2O$ (**3**).

Figure S25. IR spectra of $K_2\{Mo_3^{IV}O_4(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot 3im\cdot 4H_2O$ (**1**) and $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**).

Figure S26. IR spectrum of *trans*-$[(Mo^{V}O)_2O(H_2homocit)_2(bpy)_2]\cdot 4H_2O$ (**3**).

Figure S27. IR spectrum of $(Et_4N)[Mo^{VI}O_2Cl(H_2cit)]\cdot H_2O$ (**4**).

Figure S28. UV-vis spectra of $K_2\{Mo_3^{IV}O_4(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot 3im\cdot 4H_2O$ (**1**) and $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**).

Figure S29. UV-vis spectrum of *trans*-$[(Mo^{V}O)_2O(H_2homocit)_2(bpy)_2]\cdot 4H_2O$ (**3**).

Figure S30. Cyclic voltammogram of $K_2\{Mo_3^{IV}O_4(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot 3im\cdot 4H_2O$ (**1**) versus an Hg/Hg_2Cl_2 reference electrode in 1 mol/L Na_2SO_4 at a scan rate of 100 mV s^{-1}.

Figure S31. Cyclic voltammogram of $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**) versus an Hg/Hg_2Cl_2 reference electrode in 1 mol/L Na_2SO_4 at a scan rate of 100 mV s^{-1}.

Figure S32. Cyclic voltammogram of $(Et_4N)[Mo^{VI}O_2Cl(H_2cit)]\cdot H_2O$ (**4**) versus an Hg/Hg_2Cl_2 reference electrode in 1 mol/L Na_2SO_4 at a scan rate of 100 mV s^{-1}.

Figure S33. Mass spectrum of $[Mo^{IV}O_2(Hcit)]^{1-}$ in $(Et_4N)[Mo^{VI}O_2Cl(H_2cit)]\cdot H_2O$ (**3**).

Table S1. Selected bond distances (Å) and angles (°) within the water layers in $K_2\{Mo_3^{IV}O_4(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot 3im\cdot 4H_2O$ (**1**).

Table S2. Selected bond distances (Å) and angles (°) within the water layers in $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**).

Table S3. Selected bond distances (Å) and angles (°) within the water layers in $(Et_4N)[Mo^{VI}O_2Cl(H_2cit)]\cdot H_2O$ (**4**).

Table S4. Comparisons of selected bond distances (Å) for $K_2\{Mo_3^{IV}O_4(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot 3im\cdot 4H_2O$ (**1**), $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**), *trans*-$[(Mo^{V}O)_2O(H_2homocit)_2(bpy)_2]\cdot 4H_2O$ (**3**), $[(Mo^{V}O)_2O(H_2cit)_2(bpy)_2]\cdot 4H_2O$ (**5**),[1] $[Mo_3^{IV}SO_3(glyc)_2(im)_5]\cdot im\cdot H_2O$ (**13**),[2] $Na_2[Mo_3^{IV}SO_3(R,S\text{-lact})_3(im)_3]\cdot 10H_2O$ (**14**),[2] $[Mo_3^{IV}S_4(PPh_3)_3(Hlact)_2(lact)]$ (**15**),[3] $Mo_3^{V/VI}O_8(im)_4\cdot im\cdot H_2O$ (**18**),[4] $Mo_3^{V/VI}O_8(im)_4\cdot H_2O$ (**19**),[4] $Mo_2^{VI}O_6(im)_4$ (**20**),[5] *cis*-$Na_2[Mo_2^{V}O_4(ox)_2(im)_2]\cdot 4.5H_2O$ (**21**),[4] *cis*-$K_2[Mo_2^{V}O_4(ox)_2(im)_2]\cdot 3H_2O$ (**22**),[4] $K(Him)[Mo_3^{IV}O_4(ox)_3(im)_3]\cdot 3H_2O$ (**23**),[4] $(4\text{-MePyH})(H_3O)[Mo_3^{IV}O_4(C_2O_4)_3(4\text{-MePy})_3]\cdot H_2O$ (**24**),[6]

$(MeNC_6H_7)(H_3O)[Mo_3^{IV}O_4(C_2O_4)_3(4\text{-}MePy)_3]\cdot 1/2(4\text{-}MePy)$ (**25**),[6] $Na_2[Mo_3^{IV}O_4((O_2CCH_2)_2NCH_3)_3]\cdot 7H_2O$ (**26**),[7] $[Mo_3^{IV}O(OH)_3(Hnta)_3]\cdot Cl\cdot 3H_2O$ (**27**),[8] $(PyH)_4[Mo_4^{V}O_8Cl_4(glyc)_2]\cdot 2EtOH$ (**28**),[9] $[Mo_4^{V}O_8(glyc)_2Py_4]$ (**29**),[9] $Na_4[Mo_6^{IV}O_8(EDTA)_3]\cdot 14H_2O$ (**30**),[10] $[Mo_6^{IV}O_{10}(bpy)_4(Hnta)_2]\cdot 10H_2O$ (**31**),[11] $[Mo_6^{IV}O_{10}(R,S\text{-lact})_2(im)_{10}]\cdot 16H_2O$ (**32**),[2] $[Mo_3^{IV}SO_3(acac)_3(py)_3]\cdot PF_6\cdot 2C_6H_5CH_3$ (**33**)[12] and $[Mo_3^{IV}S_4(Clqn)_3(H_2O)_3]^+$ (**34**)[13] (HClqn = C_9H_6ClNO).

Table S5. ^{13}C NMR data of $K_2\{Mo_3^{IV}O_4(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot 3im\cdot 4H_2O$ (**1**), $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**) and $(Et_4N)[Mo^{VI}O_2Cl(H_2cit)]\cdot H_2O$ (**4**).

Table S6. Crystallographic data and structural refinements for $K_2\{Mo_3^{IV}O_4(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot 3im\cdot 4H_2O$ (**1**), $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**), *trans*-$[(Mo^{V}O)_2O(H_2homocit)_2(bpy)_2]\cdot 4H_2O$ (**3**) and $(Et_4N)[Mo^{VI}O_2Cl(H_2cit)]\cdot H_2O$ (**4**).

Table S7. Selected bond distances (Å) and angles (°) for $K_2\{Mo_3^{IV}O_4(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot 3im\cdot 4H_2O$ (**1**).

Table S8. Selected bond distances (Å) and angles (°) for $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**).

Table S9. Selected bond distances (Å) and angles (°) for *trans*-$[(Mo^{V}O)_2O(H_2homocit)_2(bpy)_2]\cdot 4H_2O$ (**3**).

Table S10. Selected bond distances (Å) and angles (°) for $(Et_4N)[Mo^{VI}O_2Cl(H_2cit)]\cdot H_2O$ (**4**).

Figure S1. Perspective view of the anion structure of $K_2\{Mo_3^{IV}O_4(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot 3im\cdot 4H_2O$ (**1**).

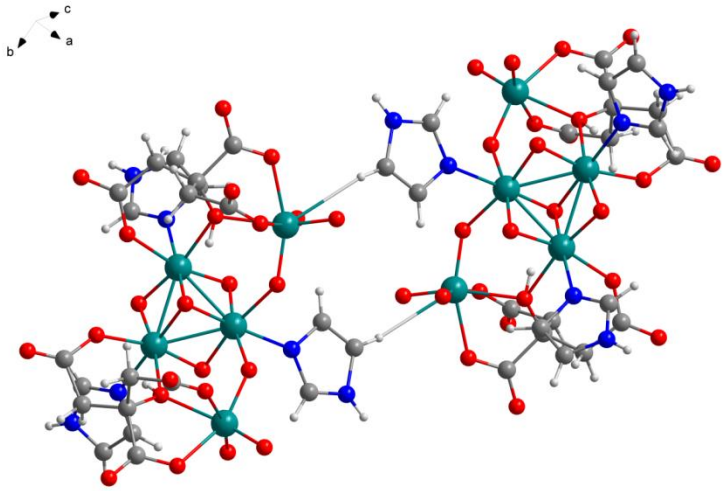

Figure S2. 2D layered structure of $K_2\{Mo_3^{IV}O_4(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot 3im\cdot 4H_2O$ (**1**).

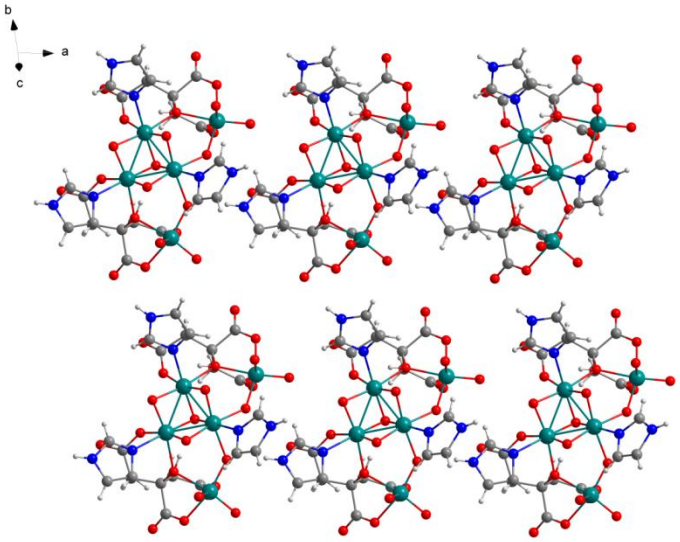

Figure S3. 2D layered structure of $K_2\{Mo_3^{IV}O_4(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot 3im\cdot 4H_2O$ (**1**) viewed along *a* axis.

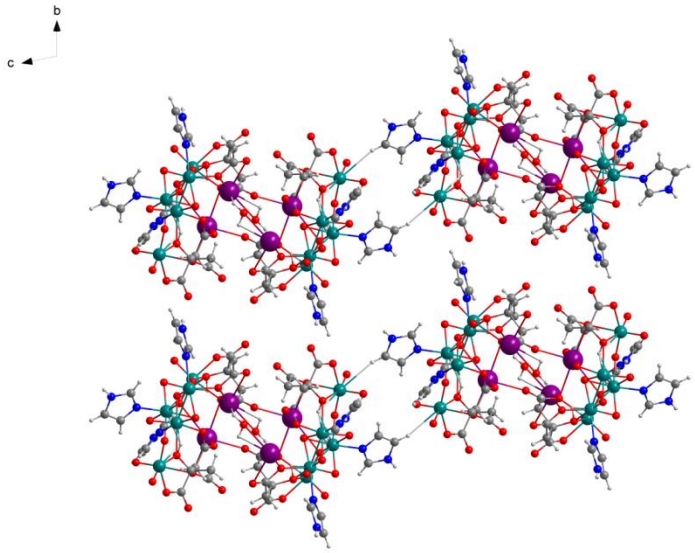

Figure S4. 2D layered structure of $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**).

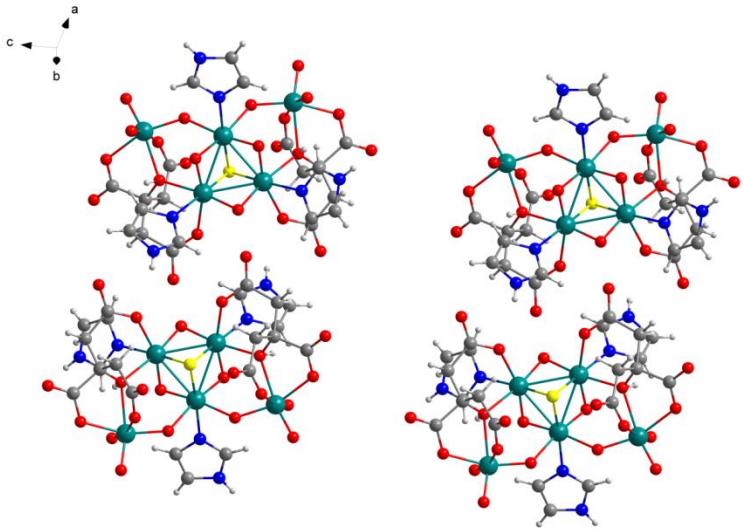

Figure S5. The 3D supramolecular are linked through hydrogen bonds in $K_2\{Mo_3^{IV}O_4(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot 3im\cdot 4H_2O$ (**1**) viewed along *a* axis.

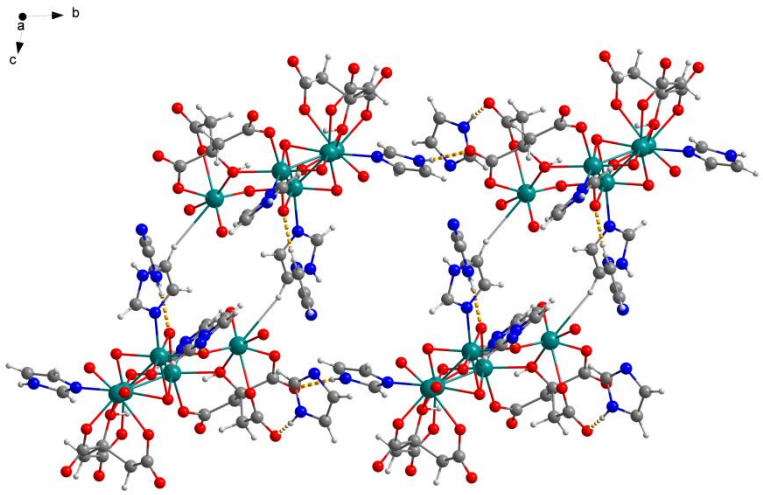

Figure S6. The 3D supramolecular are linked through hydrogen bonds in $K_2\{Mo_3^{IV}O_4(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot 3im\cdot 4H_2O$ (**1**) viewed along *b* axis.

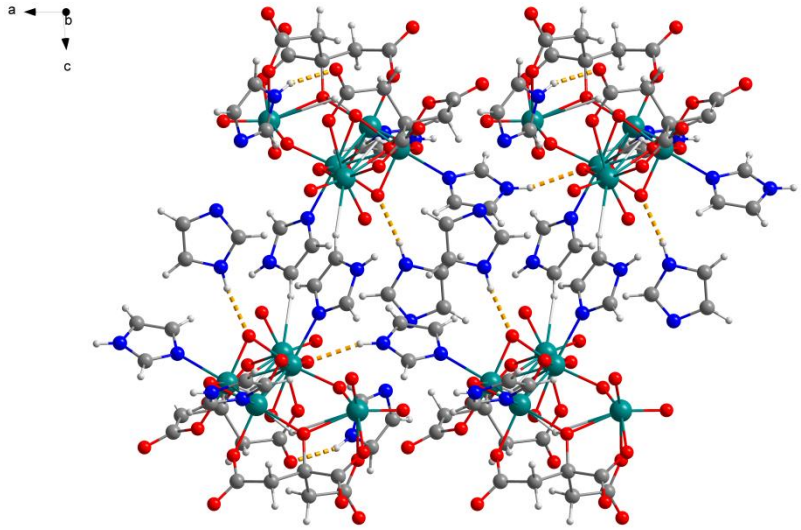

Figure S7. The 3D supramolecular are linked through hydrogen bonds in $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**).

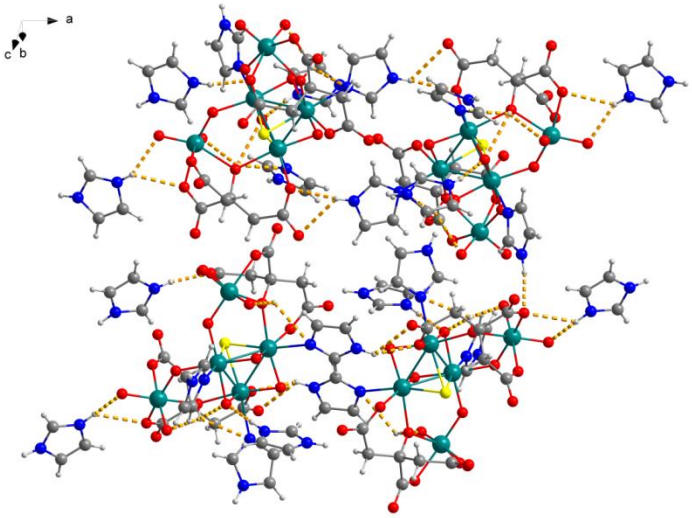

Figure S8. 3D water layers in $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**).

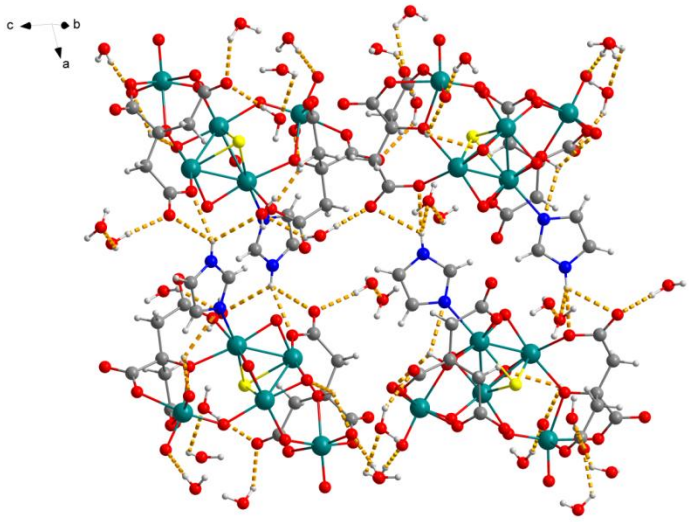

Figure S9. 2D layered structure of *trans*-[$(Mo^{V}O)_2O(H_2homocit)_2(bpy)_2$] $4H_2O$ (**3**).

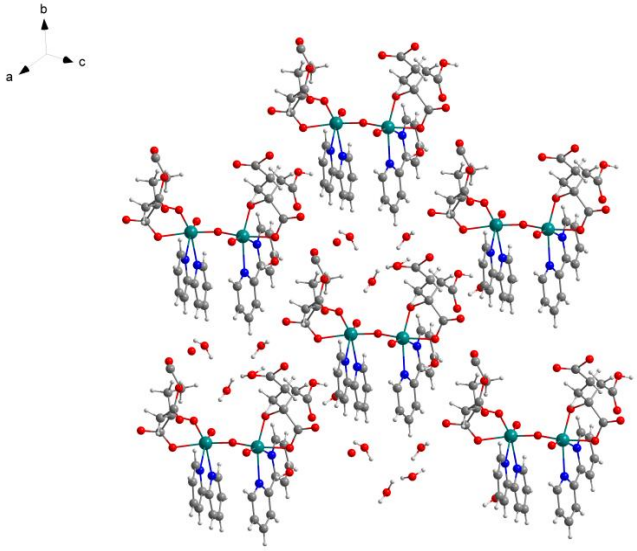

Figure S10. 2D layered structure of $(Et_4N)[Mo^{VI}O_2Cl(H_2cit)]\cdot H_2O$ (**4**).

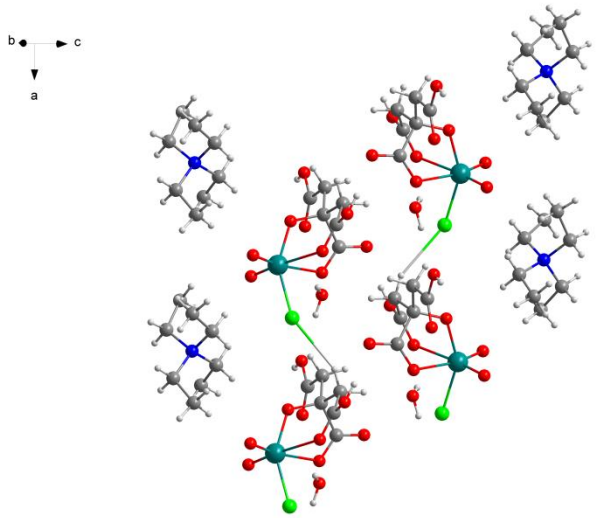

Figure S11. 2D water layers in $(Et_4N)[Mo^{VI}O_2Cl(H_2cit)]\cdot H_2O$ (**4**).

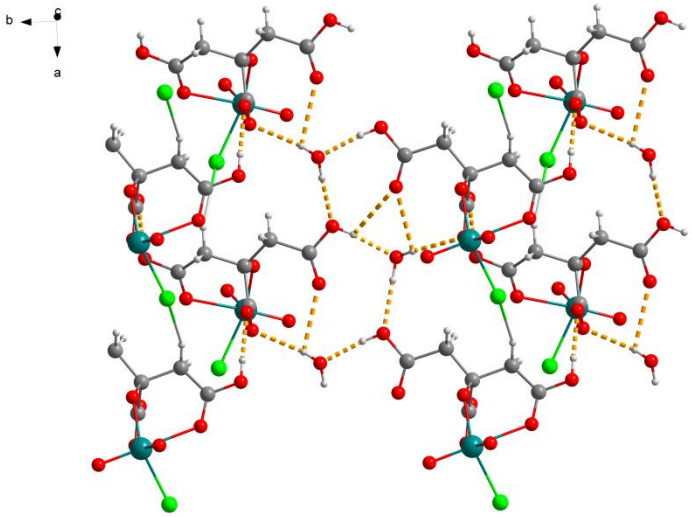

Figure S12. ^1H NMR spectrum of $K_2\{Mo_3^{IV}O_4(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot 3im\cdot 4H_2O$ (**1**).

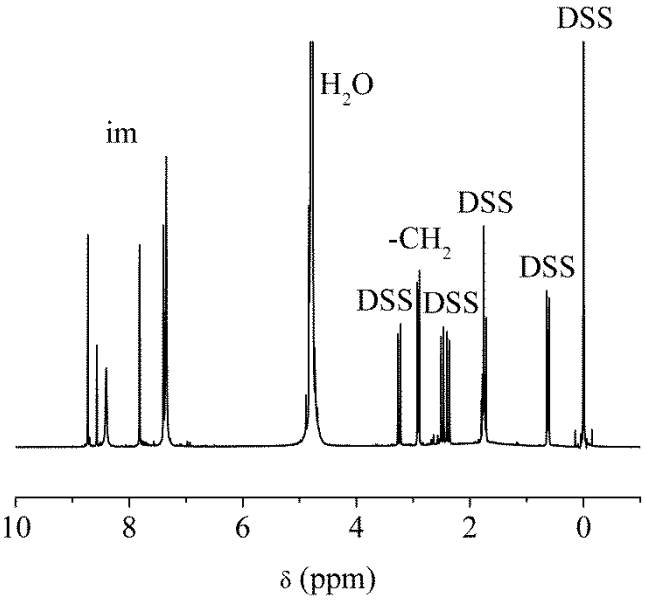

Figure S13. ^{1}H NMR spectrum of $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**).

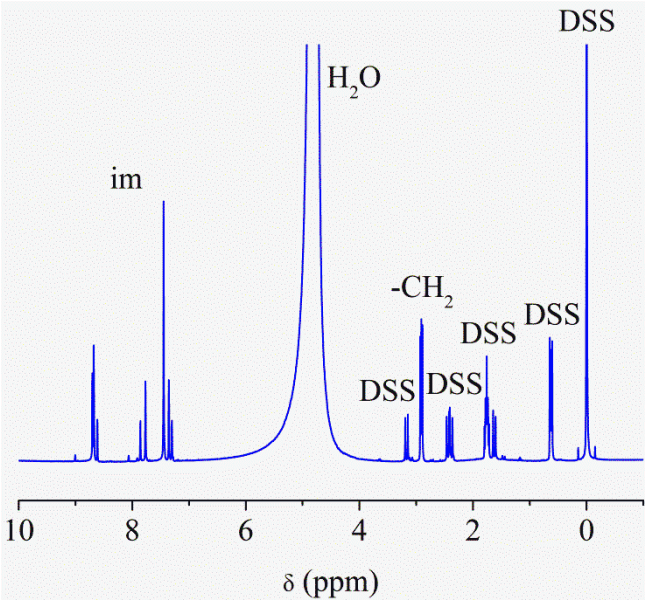

Figure S14. ^{13}C NMR spectrum of $(Et_4N)[Mo^{VI}O_2Cl(H_2cit)]\cdot H_2O$ (**4**).

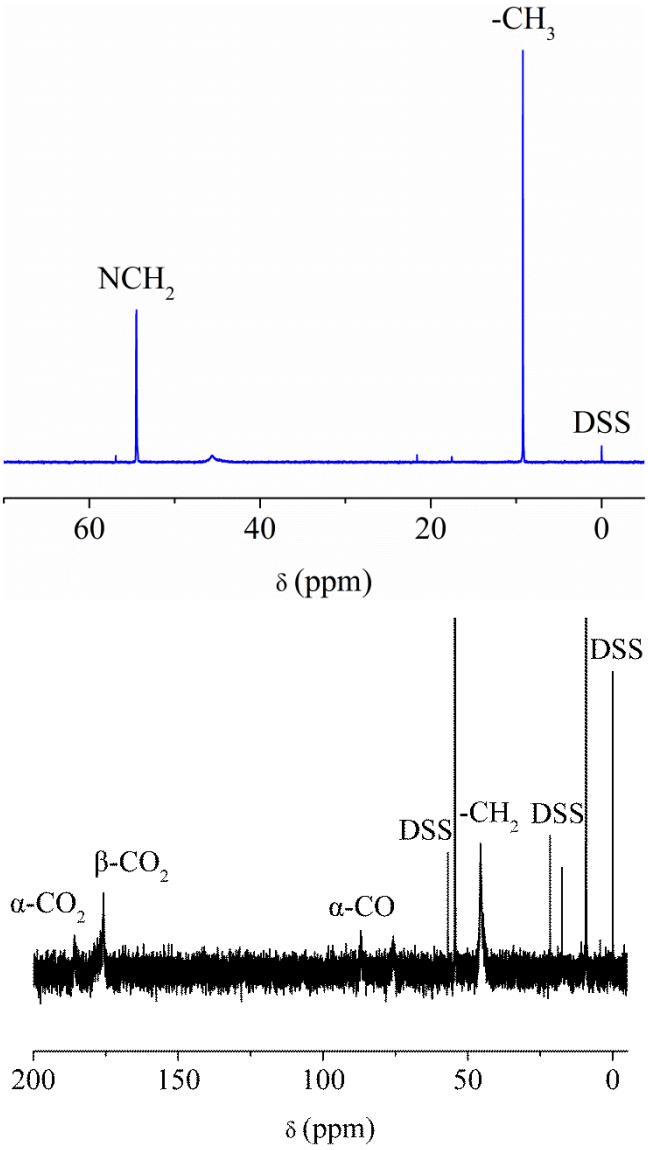

Figure S15. ^{1}H NMR spectrum of $(Et_4N)[Mo^{VI}O_2Cl(H_2cit)]\cdot H_2O$ (**4**).

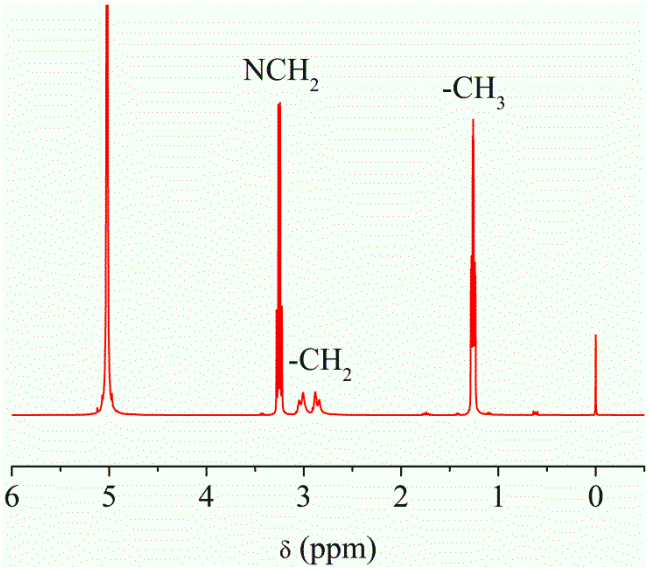

Figure S16. ^{13}C NMR spectrum of $K_2\{Mo_3^{IV}O_4(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot 3im\cdot 4H_2O$ (**1**) after three months.

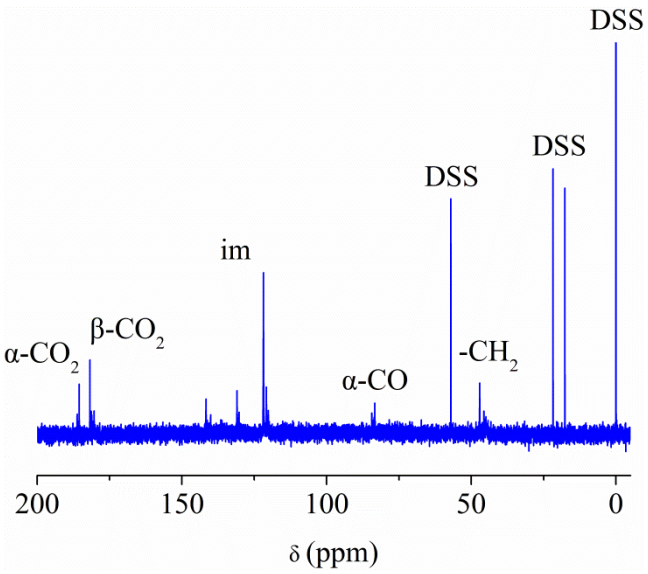

Figure S17. ^{1}H NMR spectrum of $K_2\{Mo_3^{IV}O_4(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot 3im\cdot 4H_2O$ (**1**) after three months.

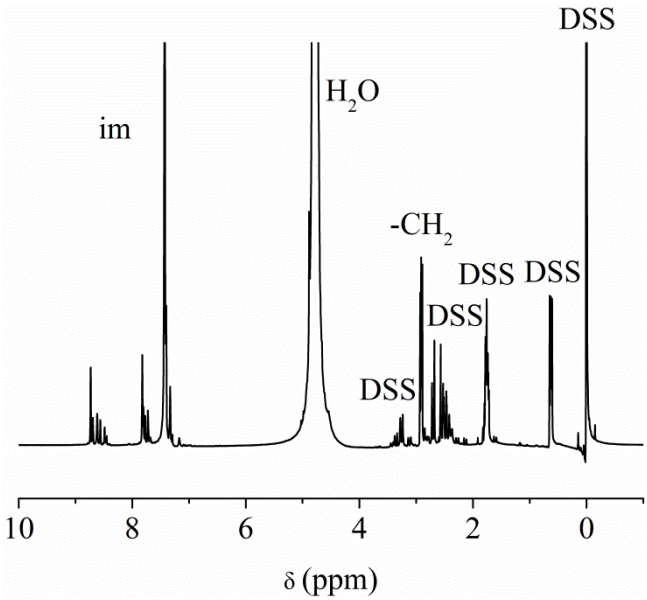

Figure S18. ^{13}C NMR spectrum of $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**) after three months.

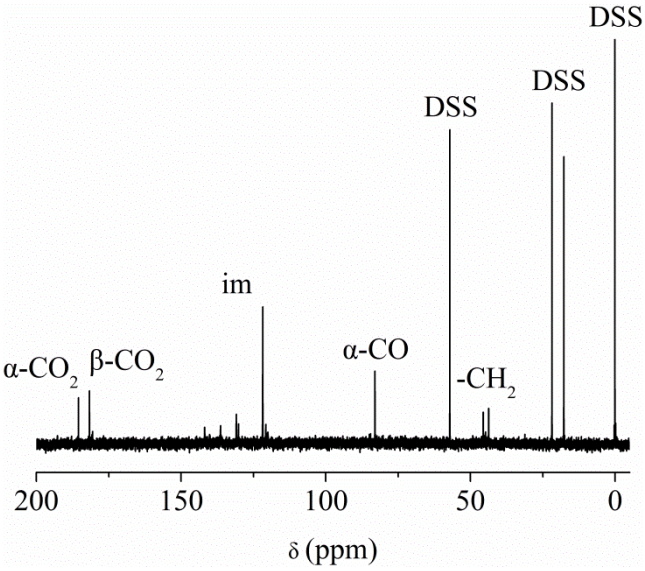

Figure S19. ^{1}H NMR spectrum of $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**) after three months.

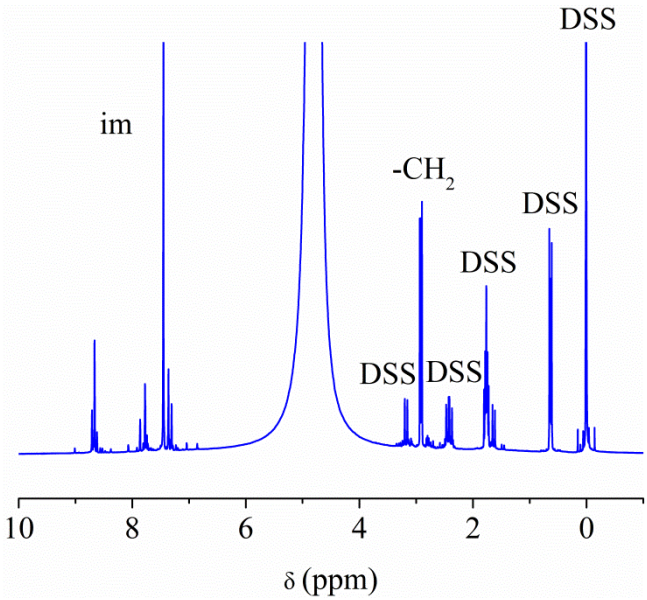

Figure S20. ^{13}C NMR spectrum of $(Et_4N)[Mo^{VI}O_2Cl(H_2cit)]\cdot H_2O$ (**4**) after three months.

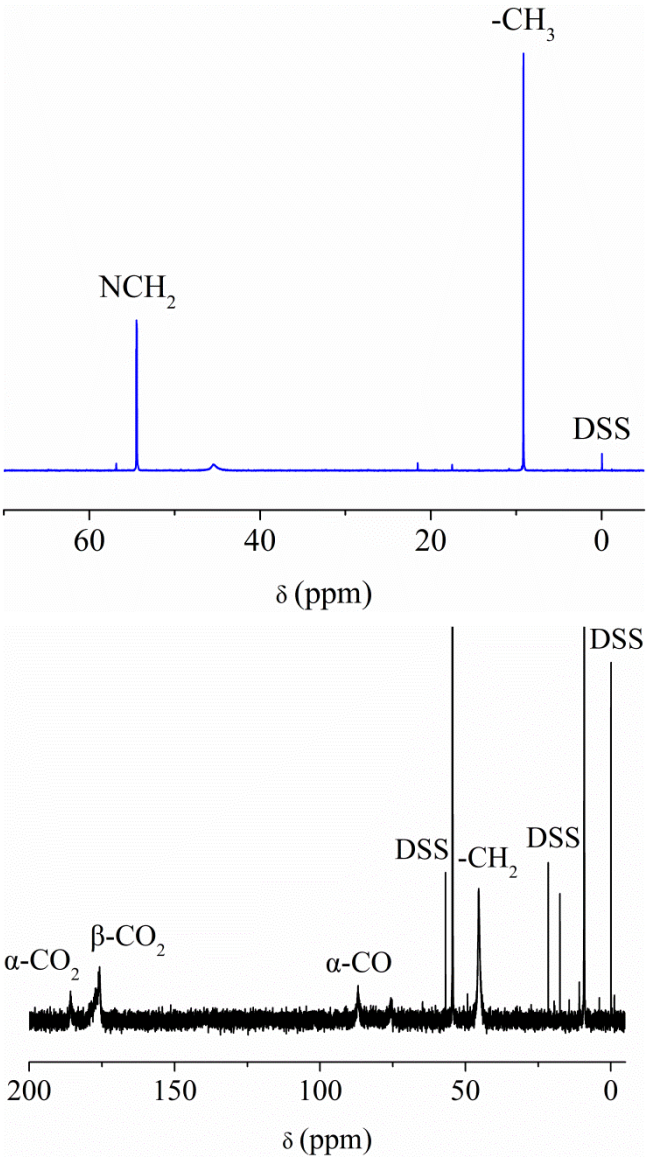

Figure S21. ^{1}H NMR spectrum of $(Et_4N)[Mo^{VI}O_2Cl(H_2cit)]\cdot H_2O$ (**4**) after three months.

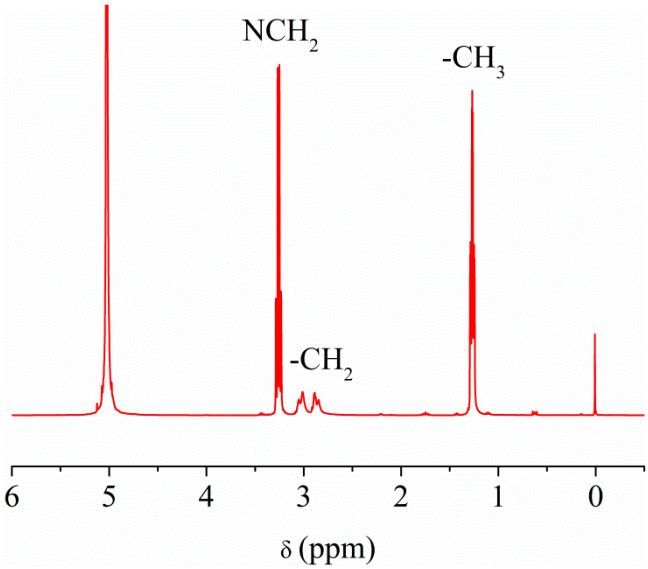

Figure S22. XPS spectrum of $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**).

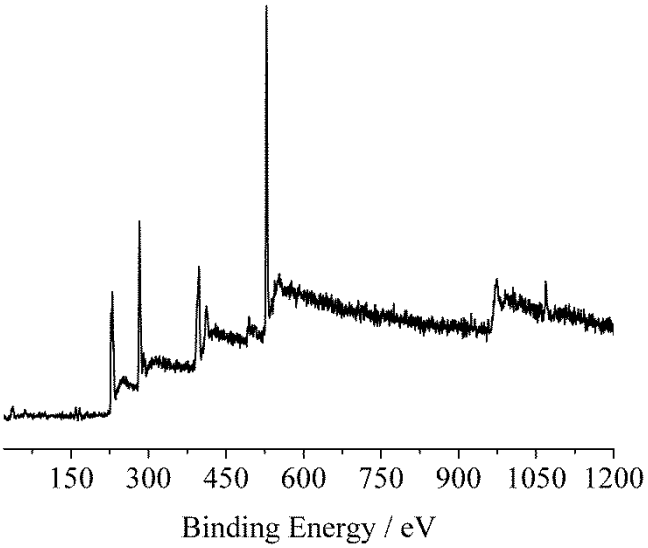

Figure S23. Plots of the experimental temperature dependence of χ_M^{-1} and $\chi_M T$ for $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**).

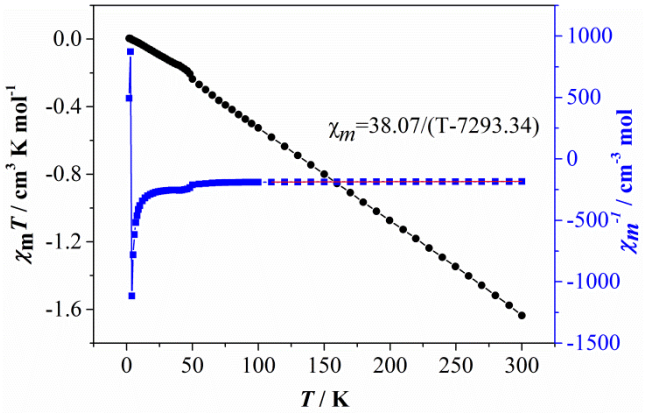

Figure S24. Plots of the experimental temperature dependence of χ_M^{-1} and $\chi_M T$ for *trans*-$[(Mo^{V}O)_2O(H_2homocit)_2(bpy)_2]\cdot 4H_2O$ (**3**).

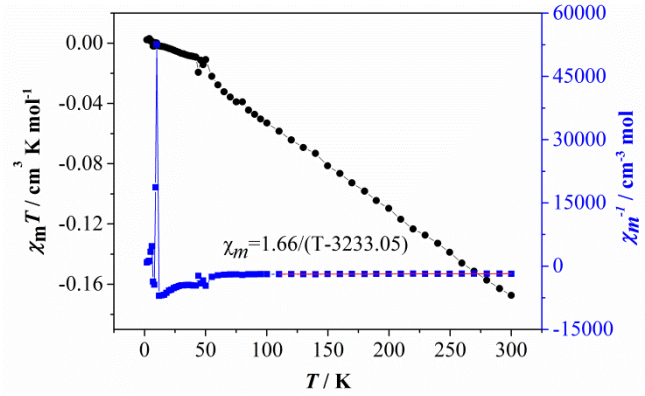

Figure S25. IR spectra of $K_2\{Mo_3^{IV}O_4(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot 3im\cdot 4H_2O$ (**1**) and $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**).

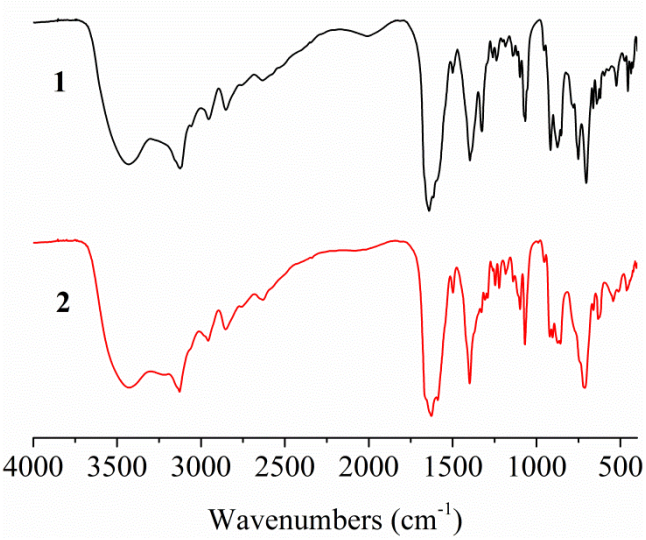

Figure S26. IR spectrum of *trans*-$[(Mo^{V}O)_2O(H_2homocit)_2(bpy)_2]\cdot 4H_2O$ (**3**).

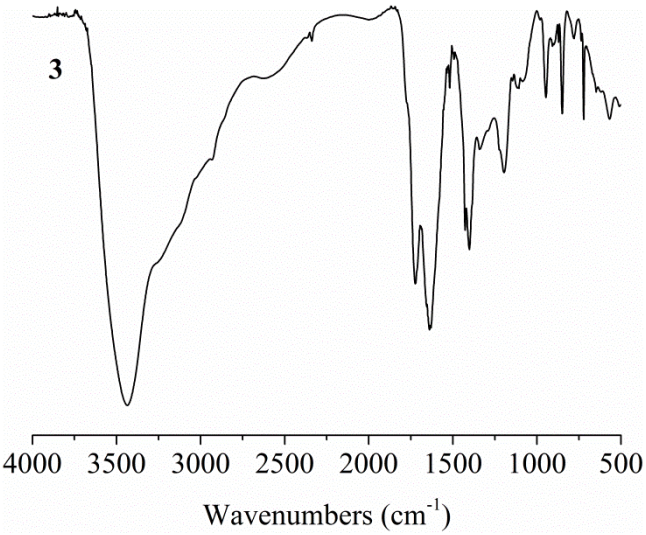

Figure S27. IR spectrum of $(Et_4N)[Mo^{VI}O_2Cl(H_2cit)]\cdot H_2O$ (**4**).

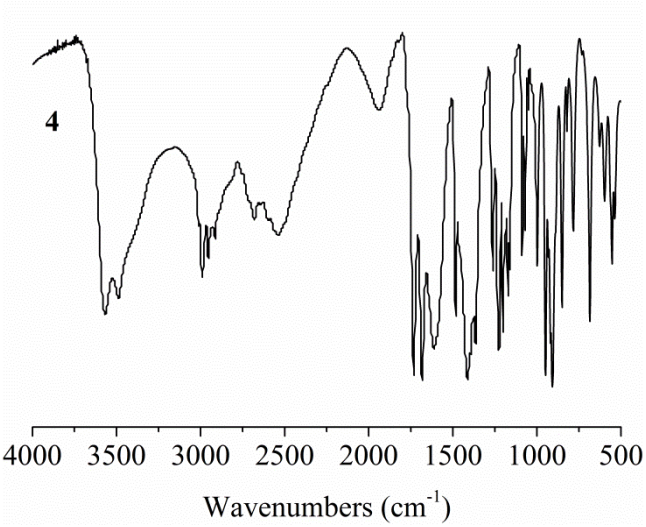

Figure S28. UV-vis spectra of $K_2\{Mo_3^{IV}O_4(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot 3im\cdot 4H_2O$ (**1**) and $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**).

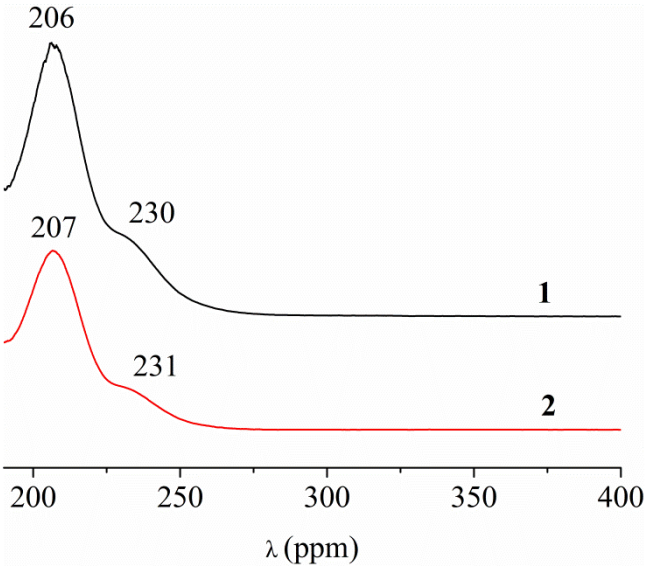

Figure S29. UV-vis spectrum of *trans*-[$(Mo^{V}O)_2O(H_2homocit)_2(bpy)_2$] $4H_2O$ (**3**).

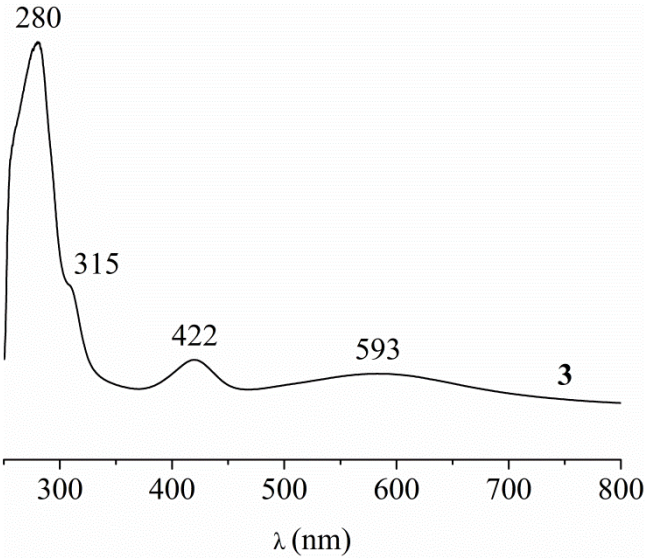

Figure S30. Cyclic voltammogram of $K_2\{Mo_3^{IV}O_4(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot 3im\cdot 4H_2O$ (**1**) versus an Hg/Hg_2Cl_2 reference electrode in 1 mol/L Na_2SO_4 at a scan rate of 100 mV s^{-1}.

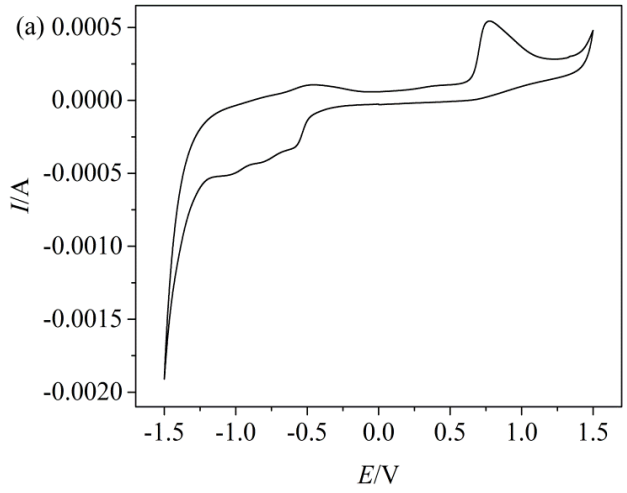

Figure S31. Cyclic voltammogram of $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**) versus an Hg/Hg_2Cl_2 reference electrode in 1 mol/L Na_2SO_4 at a scan rate of 100 mV s^{-1}.

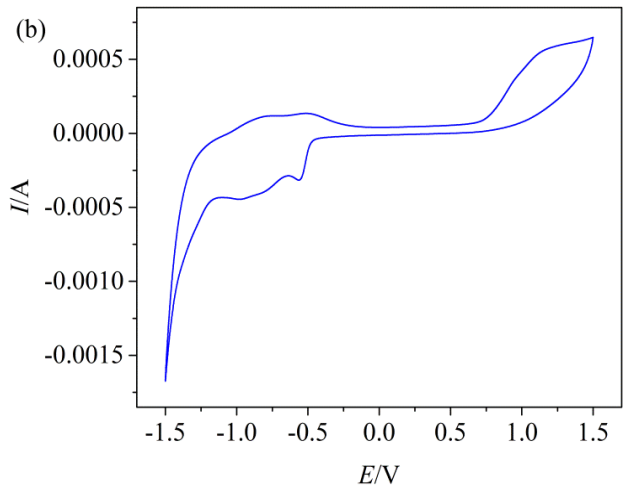

Figure S32. Cyclic voltammogram of $(Et_4N)[Mo^{VI}O_2Cl(H_2cit)]\cdot H_2O$ (**4**) versus an Hg/Hg_2Cl_2 reference electrode in 1 mol/L Na_2SO_4 at a scan rate of 100 mV s^{-1}.

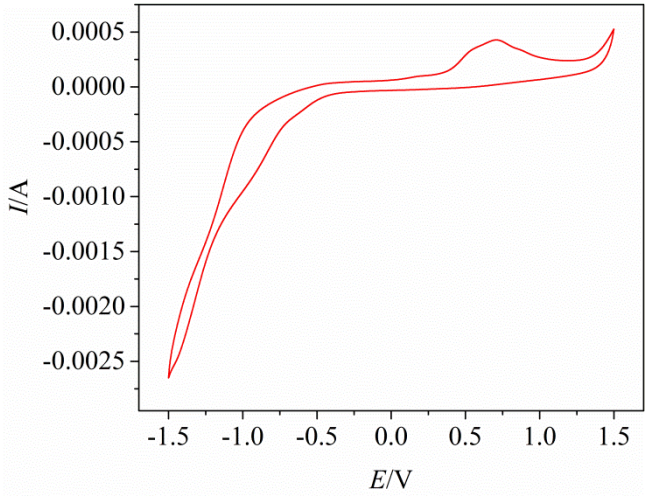

Figure S33. Mass spectrum of $[Mo^{IV}O_2(Hcit)]^{1-}$ in $(Et_4N)[Mo^{VI}O_2Cl(H_2cit)]\cdot H_2O$ (**3**).

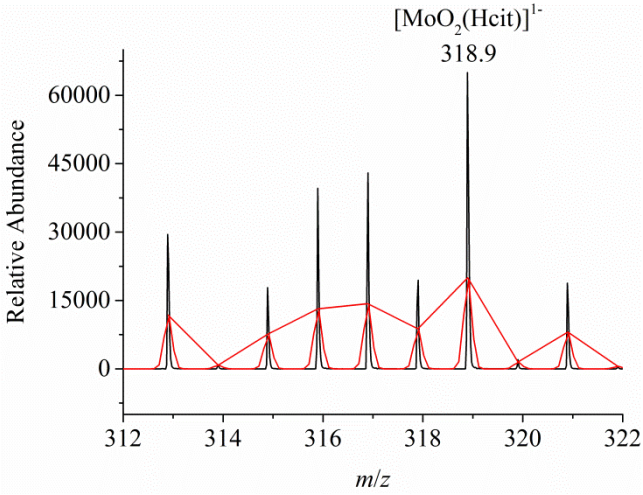

Table S1. Selected bond distances (Å) and angles (°) within the water layers in $K_2\{Mo_3^{IV}O_4(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot 3im\cdot 4H_2O$ (**1**).

D–H···A	D–H(Å)	H···A(Å)	D···A(Å)	D–H···A(°)
O_{1w}–H ··O_{6d}	0.79	2.26	3.01(1)	161
O_{2w}–H ··O_{5d}	0.91	2.29	2.94(1)	128
O_{2w}–H ··O_{5d}	0.93	2.56	2.94(1)	105
O_{3w}–H ··O_{12e}	0.85	2.41	3.20(1)	154
O_{3w}–H ··O_{13e}	0.85	2.23	2.87(1)	131
O_{3w}–H ··O_{2wa}	0.87	1.25	1.89(2)	126
O_{4wB}–H ··O_{4wBf}	0.67	1.82	2.18(1)	114
O_{4wB}–H ··O_{4wBf}	0.80	1.66	2.177(1)	121
N_4–H ··O_{10a}	0.88	2.06	2.898(7)	158
N_6–H ··O_{3b}	0.88	2.03	2.874(8)	160
N_8–H ··O_5	0.88	1.90	2.732(9)	157
N_{10}–H ··O_{22c}	0.86	1.98	2.818(8)	164

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

Table S2. Selected bond distances (Å) and angles (°) within the water layers in $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**).

D–H···A	D–H(Å)	H···A(Å)	D···A(Å)	D–H···A(°)
O_{1w}–H ··O_{2w}	0.85	1.95	2.737(8)	154
O_{1w}–H ··O_{17a}	0.82	2.03	2.822(6)	164
O_{2w}–H ··O_{3b}	0.88	1.88	2.724(9)	159
O_{2w}–H ··O_{6c}	0.82	2.21	2.918(8)	145
O_{3w}–H ··O_{9d}	0.97	1.76	2.701(8)	161
O_{3w}–H ··O_{4we}	0.87	2.38	2.969(10)	125
O_{4w}–H ··O_{3f}	0.83	2.48	2.880(6)	111
O_{4w}–H ··O_{15g}	0.84	1.93	2.767(7)	173
O_{5wA}–H ··O_9	0.85	1.93	2.719(10)	154
O_{5wA}–H ··O_{18e}	0.85	2.26	2.702(10)	112
O_{6w}–H ··N_{12}	0.85	1.91	2.725(11)	162
O_{6w}–H ··O_{15h}	0.85	2.05	2.530(8)	115
N_2–H ··O_{12e}	0.86	1.93	2.772(7)	166
N_4–H ··O_{2w}	0.86	2.55	3.116(10)	125
N_4–H ··O_{16c}	0.86	2.27	3.019(8)	146
N_4–H ··O_{17c}	0.86	2.52	3.033(8)	119
N_6–H ··O_{21d}	0.86	2.09	2.934(7)	168
N_7–H ··O_{23}	0.85	1.93	2.766(6)	164
N_8–H ··O_{1w}	0.86	1.86	2.720(8)	176
N_9–H ··O_4	0.85	1.87	2.719(6)	174
N_{10}–H ··O_{19i}	0.89	2.15	2.928(9)	146

Symmetry codes: (a) 1 – *x*, ½ + *y*, ½ – *z*; (b) 1 – *x*, ½ + *y*, 1½ – *z*; (c) 1 – *x*, 1 – *y*, 1 – *z*; (d) *x*, 1½ – *y*, -½ + *z*; (e) *x*, 1½ – *y*, ½ + *z*; (f) *x*, *y*, -1 + *z*; (g) *x*, ½ – *y*, -½ + *z*; (h) 2 – *x*, ½ + *y*, 1½ – *z*; (i) 2 – *x*, 1 – *y*, 1 – *z*

Table S3. Selected bond distances (Å) and angles (°) within the water layers in $(Et_4N)[Mo^{VI}O_2Cl(H_2cit)]\cdot H_2O$ (**4**).

D–H ··A	D–H(Å)	H···A(Å)	D···A(Å)	D–H···A(°)
O_{1w}–H ··O_{2a}	0.85	2.16	2.981(6)	164
O_{1w}–H ··O_{6a}	0.85	2.56	2.912(6)	106
O_{1w}–H ··O_{7b}	0.85	1.97	2.823(6)	178
O_5–H ··O_{3c}	0.82	1.78	2.594(6)	172
O_7–H ··O_{1w}	0.82	1.77	2.585(6)	173

Symmetry codes: (a) ½ + *x*, 1½ – *y*, 1 – *z*; (b) -½ + *x*, 1½ – *y*, 1 – *z*; (c) ½ + *x*, ½ – *y*, 1 – *z*

Table S4. Comparisons of selected bond distances (Å) for $K_2\{Mo_3^{IV}O_4(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot 3im\cdot 4H_2O$ (**1**), $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**), *trans*-$[(Mo^{V}O)_2O(H_2homocit)_2(bpy)_2]\cdot 4H_2O$ (**3**), $[(Mo^{V}O)_2O(H_2cit)_2(bpy)_2]\cdot 4H_2O$ (**5**),[1] $[Mo_3^{IV}SO_3(glyc)_2(im)_5]\cdot im\cdot H_2O$ (**13**),[2] $Na_2[Mo_3^{IV}SO_3(R,S\text{-lact})_3(im)_3]\cdot 10H_2O$ (**14**),[2] $[Mo_3^{IV}S_4(PPh_3)_3(Hlact)_2(lact)]$ (**15**),[3] $Mo_3^{V/VI}O_8(im)_4\cdot im\cdot H_2O$ (**18**),[4] $Mo_3^{V/VI}O_8(im)_4\cdot H_2O$ (**19**),[4] $Mo_2^{VI}O_6(im)_4$ (**20**),[5] *cis*-$Na_2[Mo_2^{V}O_4(ox)_2(im)_2]\cdot 4.5H_2O$ (**21**),[4] *cis*-$K_2[Mo_2^{V}O_4(ox)_2(im)_2]\cdot 3H_2O$ (**22**),[4] $K(Him)[Mo_3^{IV}O_4(ox)_3(im)_3]\cdot 3H_2O$ (**23**),[4] $(4\text{-}MePyH)(H_3O)[Mo_3^{IV}O_4(C_2O_4)_3(4\text{-}MePy)_3]\cdot H_2O$ (**24**),[6] $(MeNC_6H_7)(H_3O)[Mo_3^{IV}O_4(C_2O_4)_3(4\text{-}MePy)_3]\cdot 1/2(4\text{-}MePy)$ (**25**),[6] $Na_2[Mo_3^{IV}O_4((O_2CCH_2)_2NCH_3)_3]\cdot 7H_2O$ (**26**),[7] $[Mo_3^{IV}O(OH)_3(Hnta)_3]\cdot Cl\cdot 3H_2O$ (**27**),[8] $(PyH)_4[Mo_4^{V}O_8Cl_4(glyc)_2]\cdot 2EtOH$ (**28**),[9] $[Mo_4^{V}O_8(glyc)_2Py_4]$ (**29**),[9] $Na_4[Mo_6^{IV}O_8(EDTA)_3]\cdot 14H_2O$ (**30**),[10] $[Mo_6^{IV}O_{10}(bpy)_4(Hnta)_2]\cdot 10H_2O$ (**31**),[11] $[Mo_6^{IV}O_{10}(R,S\text{-lact})_2(im)_{10}]\cdot 16H_2O$ (**32**),[2] $[Mo_3^{IV}SO_3(acac)_3(py)_3]\cdot PF_6\cdot 2C_6H_5CH_3$ (**33**)[12] and $[Mo_3^{IV}S_4(Clqn)_3(H_2O)_3]^+$ (**34**)[13] (HClqn = C_9H_6ClNO).

Complexes[a] (Mo^{n+})	Mo–N	Mo–μ_2-O/S	Mo–Mo	Mo–μ_3-O/S
1(IV/VI)	$2.199(6)_{av}$	$1.922(4)_{av}$(IV) $2.045(4)_{av}$(IV) $1.838(4)_{av}$(VI)	$2.508(1)_{av}$	$2.042(4)_{av}$
2(IV/VI)	$2.199(5)_{av}$	$1.930(4)_{av}$(IV) $2.032(4)_{av}$(IV) $1.824(4)_{av}$(VI)	$2.593(1)_{av}$	$2.367(1)_{av}$
3(V)	$2.273(2)_{av}$	$1.867(1)_{av}$		
5(V)[1]	$2.307(4)_{av}$	$1.882(3)_{av}$		
18(V/VI)[4]	$2.201(5)_{av}$	$1.947(4)_{av}$	2.573(1)	
19(V/VI)[4]	$2.203(5)_{av}$	$1.952(4)_{av}$	2.573(1)	
20(VI)[5]	$2.225(4)_{av}$	$1.940(3)_{av}$		
21(V)[4]	$2.186(3)_{av}$	$1.938(3)_{av}$	2.560(1)	
22(V)[4]	$2.187(3)_{av}$	$1.940(3)_{av}$	2.548 (1)	
23(IV)[4]	$2.184(6)_{av}$	$1.910(4)_{av}$	$2.494(1)_{av}$	$2.030(4)_{av}$
24(IV)[6]		$1.914(3)_{av}$	$2.499(5)_{av}$	$2.038(3)_{av}$
25(IV)[6]		$1.927(2)_{av}$	$2.503(3)_{av}$	$2.038(2)_{av}$
26(IV)[7]	$2.231(5)_{av}$	$1.918(4)_{av}$	$2.495(1)_{av}$	$2.043(4)_{av}$
27(IV)[8]	$2.23(1)_{av}$	$1.903(8)_{av}$	$2.482(1)_{av}$	$2.046(8)_{av}$
28(V)[9]		$1.935(3)_{av}$	2.612(1)	$2.095(3)_{av}$
29(V)[9]	$2.226(4)_{av}$	$1.926(3)_{av}$	2.588(1)	$2.085(3)_{av}$
30(IV)[10]	$2.274(9)_{av}$	$1.920(7)_{av}$	$2.506(1)_{av}$	$2.042(7)_{av}$
31(IV)[11]	$2.227(4)_{av}$	$1.946(3)_{av}$	$2.532(2)_{av}$	$2.050(3)_{av}$
32(IV)[2]	$2.206(6)_{av}$	$1.946(6)_{av}$	$2.529(1)_{av}$	$2.047(4)_{av}$
33(IV)[12]	$2.246(6)_{av}$	$1.930(5)_{av}$	$2.594(1)_{av}$	$2.364(2)_{av}$
13(IV)[2]	$2.223(3)_{av}$	$1.929(2)_{av}$	$2.610(1)_{av}$	$2.360(1)_{av}$

14(IV)[2]	$2.243(8)_{av}$	$1.936(6)_{av}$	$2.612(1)_{av}$	$2.369(2)_{av}$
34(IV)[13]	$2.229(4)_{av}$	$2.301(1)_{av}$	$2.766(1)_{av}$	$2.345(1)_{av}$
15(IV)[3]		$2.296(1)_{av}$	$2.761(1)_{av}$	$2.363(1)_{av}$

Table S5. ^{13}C NMR data of $K_2\{Mo_3^{IV}O_4(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot 3im\cdot 4H_2O$ (**1**), $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**) and $(Et_4N)[Mo^{VI}O_2Cl(H_2cit)]\cdot H_2O$ (**4**).

Complex	α-hydroxy/alkoxy	α-carboxy	β-carboxy	methylene
1	83.5	185.5	181.3	45.2
2	82.9	185.4	181.7	44.5
4	87.0	185.8	175.8	45.6

Table S6. Crystallographic data and structural refinements for $K_2\{Mo_3^{IV}O_4(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot 3im\cdot 4H_2O$ (**1**), $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**), *trans*-$[(Mo^{V}O)_2O(H_2homocit)_2(bpy)_2]\cdot 4H_2O$ (**3**) and $(Et_4N)[Mo^{VI}O_2Cl(H_2cit)]\cdot H_2O$ (**4**).

Identification code	**1**	**2**
Empirical formula	$C_{30}H_{42}K_2Mo_5N_{12}O_{28}$	$C_{30}H_{48}Mo_5N_{12}O_{29}S$
Formula weight	1576.62	1552.53
Temperature/K	173.0	173.0
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	9.7975(3)	21.9484(4)
b/Å	13.8912(7)	15.2878(3)
c/Å	18.5268(8)	15.5230(3)
α/ °	100.570(4)	90
β/ °	94.254(3)	103.660(2)
γ/ °	101.331(4)	90
Volume/Å^3	2414.4(2)	5061.3 (2)
Z	2	4
d_{calc} g/cm^3	2.163	2.030
μ/mm^{-1}	12.849	11.190
F(000)	1548.0	3056.0
Crystal size/mm^3	0.24 × 0.08 × 0.04	0.3 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2θrange for data collection/ °	6.626 to 124.324	7.114 to 124.368
Index ranges	-5 ≤ h ≤ 11, -15 ≤ k ≤ 15, -21 ≤ l ≤ 21	-25 ≤ h ≤ 25, -14 ≤ k ≤ 17, -17 ≤ l ≤ 17
Reflections collected	13938	16632

	7516	7914
Independent reflections	[R_{int} = 0.0337, R_{sigma} = 0.0465]	[R_{int} = 0.0331, R_{sigma} = 0.0422]
Data/restraints/parameters	7516/55/685	7914/23/679
Goodness–of–fit on F^2	1.046	1.052
Final R indexes [I ≥ 2σ (I)]	R_1 = 0.0465, wR_2 = 0.1276	R_1 = 0.0446, wR_2 = 0.1137
Final R indexes [all data]	R_1 = 0.0487, wR_2 = 0.1299	R_1 = 0.0462, wR_2 = 0.1153
Largest diff. peak/hole / e ·Å^{-3}	2.99/-1.47	2.76/-1.54
Flack parameter		

Identification code	**3**	**4**
Empirical formula	$C_{34}H_{40}Mo_2N_4O_{21}$	$C_{14}H_{28}NO_{10}MoCl$
Formula weight	1032.58	501.77
Temperature/K	173	173.0(1)
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$	$P\ 2_12_12_1$
a/Å	11.669 (2)	7.6683(3)
b/Å	13.252(1)	12.0711(3)
c/Å	15.392(2)	22.2111(6)
α/ °	97.117(9)	90
β/ °	104.18(1)	90
γ/ °	115.42(1)	90
Volume/Å^3	2011.8(5)	2056.0(1)
Z	2	4
d_{calc} g/cm^3	1.685	1.621
μ/mm^{-1}	5.900	0.817

$F(000)$	1024.0	1032.0
Crystal size/mm^3	0.1 × 0.1 × 0.01	0.4 × 0.1 × 0.08
Radiation	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)
2θrange for data collection/ °	6.136 to 124.508	6.456 to 59.114
Index ranges	-13 ≤ h ≤ 13, -10 ≤ k ≤ 15, -17 ≤ l ≤ 17	–10 ≤ h ≤ 7, –16 ≤ k ≤ 13, –30 ≤ l ≤ 11
Reflections collected	11637	6054
Independent reflections	6264 [*R*int = 0.0686, *R*sigma = 0.1034]	4183 [R_{int} = 0.0418, R_{sigma} = 0.0868]
Data/restraints/parameters	6264/4/500	4183/0/253
Goodness–of–fit on F^2	1.037	1.059
Final *R* indexes [I ≥ 2σ (*I*)]	*R*1 = 0.0769, w*R*2 = 0.2138	R_1 = 0.0505, wR_2 = 0.0805
Final *R* indexes [all data]	*R*1 = 0.1083, w*R*2 = 0.2387	R_1 = 0.0618, wR_2 = 0.0857
Largest diff. peak/hole / e ·Å^{-3}	2.44/-0.99	0.78/–0.70
Flack parameter		0.03(6)

Table S7. Selected bond distances (Å) and angles (°) for $K_2\{Mo_3^{IV}O_4(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot 3im\cdot 4H_2O$ (**1**).

Mo(1)–Mo(2)	2.5037(7)	Mo(3)–O(21)	2.047(4)
Mo(1)–Mo(3)	2.5010(6)	Mo(3)–O(23)	1.917(4)
Mo(1)–O(10)	2.063(4)	Mo(3)–O(24)	1.907(4)
Mo(1)–O(20)	2.027(4)	Mo(3)–N(5)	2.201(6)
Mo(1)–O(21)	2.046(4)	Mo(4)–O(1)	2.185(4)
Mo(1)–O(22)	1.946(4)	Mo(4)–O(2)	2.104(5)
Mo(1)–O(24)	1.934(4)	Mo(4)–O(4)	2.266(4)
Mo(1)–N(1)	2.196(5)	Mo(4)–O(8)	1.727(4)
Mo(2)–Mo(3)	2.5201(7)	Mo(4)–O(9)	1.707(5)
Mo(2)–O(1)	2.156(4)	Mo(4)–O(10)	1.836(4)
Mo(2)–O(6)	2.080(5)	Mo(5)–O(11)	2.198(4)
Mo(2)–O(21)	2.032(4)	Mo(5)–O(12)	2.097(4)
Mo(2)–O(22)	1.913(4)	Mo(5)–O(14)	2.251(5)
Mo(2)–O(23)	1.914(4)	Mo(5)–O(18)	1.720(5)
Mo(2)–N(3)	2.199(6)	Mo(5)–O(19)	1.718(5)
Mo(3)–O(11)	2.145(4)	Mo(5)–O(20)	1.840(4)
Mo(3)–O(16)	2.062(4)		
Mo(2)–Mo(1)–Mo(3)	60.47(2)	O(21)–Mo(3)–Mo(1)	52.3(1)
O(10)–Mo(1)–Mo(2)	94.6(1)	O(21)–Mo(3)–Mo(2)	51.6(1)
O(10)–Mo(1)–Mo(3)	141.5(1)	O(21)–Mo(3)–O(23)	99.0(2)
O(10)–Mo(1)–O(20)	86.2(2)	O(21)–Mo(3)–O(24)	101.6(2)
O(10)–Mo(1)–O(21)	89.3(2)	O(21)–Mo(3)–N(5)	173.8(2)
O(10)–Mo(1)–O(22)	88.4(2)	O(23)–Mo(3)–Mo(1)	96.1(1)
O(10)–Mo(1)–O(24)	169.4(2)	O(23)–Mo(3)–Mo(2)	48.8(1)
O(10)–Mo(1)–N(1)	83.0(2)	O(23)–Mo(3)–O(24)	96.5(2)
O(20)–Mo(1)–Mo(2)	140.1(1)	O(23)–Mo(3)–N(5)	85.2(2)
O(20)–Mo(1)–Mo(3)	95.4(1)	O(24)–Mo(3)–Mo(1)	49.8(1)
O(20)–Mo(1)–O(21)	88.3(2)	O(24)–Mo(3)–Mo(2)	94.4(1)
O(20)–Mo(1)–O(22)	169.8(2)	O(24)–Mo(3)–N(5)	82.4(2)
O(20)–Mo(1)–O(24)	90.7(2)	N(5)–Mo(3)–Mo(1)	132.1(2)
O(20)–Mo(1)–N(1)	85.7(2)	N(5)–Mo(3)–Mo(2)	133.4(2)
O(21)–Mo(1)–Mo(2)	51.9(1)	O(1)–Mo(4)–O(2)	73.0(2)
O(21)–Mo(1)–Mo(3)	52.3(1)	O(1)–Mo(4)–O(4)	78.4(2)
O(21)–Mo(1)–O(22)	100.3(2)	O(1)–Mo(4)–O(8)	158.7(2)
O(21)–Mo(1)–O(24)	100.7(2)	O(1)–Mo(4)–O(9)	91.8(2)
O(21)–Mo(1)–N(1)	170.6(2)	O(1)–Mo(4)–O(10)	89.0(2)
O(22)–Mo(1)–Mo(2)	49.0(1)	O(2)–Mo(4)–O(4)	77.8(2)
O(22)–Mo(1)–Mo(3)	94.2(1)	O(2)–Mo(4)–O(8)	90.1(2)
O(22)–Mo(1)–O(24)	93.0(2)	O(2)–Mo(4)–O(9)	92.7(2)
O(22)–Mo(1)–N(1)	85.1(2)	O(2)–Mo(4)–O(10)	156.2(2)
O(24)–Mo(1)–Mo(2)	94.3(1)	O(4)–Mo(4)–O(8)	85.6(2)

O(24)–Mo(1)–Mo(3)	48.9(1)	O(4)–Mo(4)–O(9)	168.0(2)
O(24)–Mo(1)–N(1)	86.6(2)	O(4)–Mo(4)–O(10)	83.4(2)
N(1)–Mo(1)–Mo(2)	134.0(2)	O(8)–Mo(4)–O(9)	101.9(2)
N(1)–Mo(1)–Mo(3)	135.5(2)	O(8)–Mo(4)–O(10)	103.1(2)
Mo(1)–Mo(2)–Mo(3)	59.71(2)	O(9)–Mo(4)–O(10)	103.6(2)
O(1)–Mo(2)–Mo(1)	94.3(1)	O(11)–Mo(5)–O(12)	73.3(2)
O(1)–Mo(2)–Mo(3)	140.2(1)	O(11)–Mo(5)–O(14)	77.3(2)
O(1)–Mo(2)–O(6)	81.5(2)	O(11)–Mo(5)–O(18)	157.6(2)
O(1)–Mo(2)–O(21)	88.4(2)	O(11)–Mo(5)–O(19)	93.1(2)
O(1)–Mo(2)–O(22)	88.7(2)	O(11)–Mo(5)–O(20)	88.4(2)
O(1)–Mo(2)–O(23)	169.4(2)	O(12)–Mo(5)–O(14)	78.4(2)
O(1)–Mo(2)–N(3)	85.5(2)	O(12)–Mo(5)–O(18)	90.9(2)
O(6)–Mo(2)–Mo(1)	140.1(1)	O(12)–Mo(5)–O(19)	92.4(2)
O(6)–Mo(2)–Mo(3)	99.5(1)	O(12)–Mo(5)–O(20)	157.1(2)
O(6)–Mo(2)–O(21)	87.8(2)	O(14)–Mo(5)–O(18)	84.2(2)
O(6)–Mo(2)–O(22)	166.1(2)	O(14)–Mo(5)–O(19)	168.2(2)
O(6)–Mo(2)–O(23)	91.9(2)	O(14)–Mo(5)–O(20)	84.4(2)
O(6)–Mo(2)–N(3)	84.5(2)	O(18)–Mo(5)–O(19)	103.5(2)
O(21)–Mo(2)–Mo(1)	52.4(1)	O(18)–Mo(5)–O(20)	102.2(2)
O(21)–Mo(2)–Mo(3)	52.1(1)	O(19)–Mo(5)–O(20)	102.4(2)
O(21)–Mo(2)–O(22)	101.9(2)	Mo(1)–O(21)–Mo(2)	75.8(2)
O(21)–Mo(2)–O(23)	99.7(2)	Mo(1)–O(22)–Mo(2)	80.9(2)
O(21)–Mo(2)–N(3)	170.8(2)	Mo(1)–O(21)–Mo(3)	75.4(2)
O(22)–Mo(2)–Mo(1)	50.1(1)	Mo(1)–O(24)–Mo(3)	81.3(2)
O(22)–Mo(2)–Mo(3)	94.4(1)	Mo(1)–O(10)–Mo(4)	131.5(2)
O(22)–Mo(2)–O(23)	96.3(2)	Mo(1)–O(20)–Mo(5)	131.6(2)
O(22)–Mo(2)–N(3)	84.9(2)	Mo(2)–O(21)–Mo(3)	76.3(2)
O(23)–Mo(2)–Mo(1)	96.1(1)	Mo(2)–O(23)–Mo(3)	82.3(2)
O(23)–Mo(2)–Mo(3)	48.9(1)	Mo(2)–O(1)–Mo(4)	119.6(2)
O(23)–Mo(2)–N(3)	85.6(2)	Mo(3)–O(11)–Mo(5)	120.1(2)
N(3)–Mo(2)–Mo(1)	135.0(2)	C(1)–O(1)–Mo(2)	125.0(4)
N(3)–Mo(2)–Mo(3)	134.3(1)	C(1)–O(1)–Mo(4)	113.5(4)
Mo(1)–Mo(3)–Mo(2)	59.82(2)	C(2)–O(2)–Mo(4)	120.7(4)
O(11)–Mo(3)–Mo(1)	93.6(1)	C(4)–O(4)–Mo(4)	133.2(4)
O(11)–Mo(3)–Mo(2)	138.8(1)	C(6)–O(6)–Mo(2)	127.9(4)
O(11)–Mo(3)–O(16)	82.0(2)	C(7)–O(11)–Mo(3)	125.6(4)
O(11)–Mo(3)–O(21)	87.5(2)	C(7)–O(11)–Mo(5)	113.1(4)
O(11)–Mo(3)–O(23)	170.3(2)	C(8)–O(12)–Mo(5)	120.4(4)
O(11)–Mo(3)–O(24)	89.2(2)	C(10)–O(14)–Mo(5)	135.0(4)
O(11)–Mo(3)–N(5)	87.8(2)	C(12)–O(16)–Mo(3)	131.9(4)
O(16)–Mo(3)–Mo(1)	141.6(1)	C(13)–N(1)–Mo(1)	128.8(5)
O(16)–Mo(3)–Mo(2)	99.7(1)	C(15)–N(1)–Mo(1)	124.8(5)
O(16)–Mo(3)–O(21)	89.3(2)	C(16)–N(3)–Mo(2)	125.7(5)
O(16)–Mo(3)–O(23)	90.9(2)	C(18)–N(3)–Mo(2)	127.0(4)

O(16)–Mo(3)–O(24)	165.7(2)	C(19)–N(5)–Mo(3)	128.2(5)
O(16)–Mo(3)–N(5)	86.1(2)	C(21)–N(5)–Mo(3)	125.4(4)

Table S8. Selected bond distances (Å) and angles (°) for $(Him)_2\{Mo_3^{IV}SO_3(im)_3[Mo^{VI}O_3(Hcit)]_2\}\cdot im\cdot 6H_2O$ (**2**).

Mo(1)–Mo(2)	2.5831(6)	Mo(3)–O(22)	1.946(4)
Mo(1)–Mo(3)	2.5882(6)	Mo(3)–O(23)	1.898(4)
Mo(1)–O(10)	2.023(4)	Mo(3)–N(5)	2.217(5)
Mo(1)–O(20)	2.041(4)	Mo(3)–S(1)	2.363(1)
Mo(1)–O(21)	1.950(4)	Mo(4)–O(1)	2.194(4)
Mo(1)–O(23)	1.936(4)	Mo(4)–O(2)	2.103(4)
Mo(1)–N(1)	2.185(5)	Mo(4)–O(4)	2.320(4)
Mo(1)–S(1)	2.371(1)	Mo(4)–O(8)	1.708(4)
Mo(2)–Mo(3)	2.6066(6)	Mo(4)–O(9)	1.733(4)
Mo(2)–O(1)	2.187(4)	Mo(4)–O(10)	1.825(4)
Mo(2)–O(6)	2.071(4)	Mo(5)–O(11)	2.208(4)
Mo(2)–O(21)	1.898(4)	Mo(5)–O(12)	2.104(4)
Mo(2)–O(22)	1.953(4)	Mo(5)–O(14)	2.218(4)
Mo(2)–N(3)	2.195(5)	Mo(5)–O(18)	1.717(4)
Mo(2)–S(1)	2.366(1)	Mo(5)–O(19)	1.724(4)
Mo(3)–O(11)	2.191(4)	Mo(5)–O(20)	1.823(4)
Mo(3)–O(16)	2.086(4)		
Mo(2)–Mo(1)–Mo(3)	60.54(2)	O(22)–Mo(3)–Mo(1)	96.0(1)
O(10)–Mo(1)–Mo(2)	95.3(1)	O(22)–Mo(3)–Mo(2)	48.2(1)
O(10)–Mo(1)–Mo(3)	145.5(1)	O(22)–Mo(3)–O(23)	96.0(2)
O(10)–Mo(1)–O(20)	91.3(2)	O(22)–Mo(3)–N(5)	86.1(2)
O(10)–Mo(1)–O(21)	87.6(2)	O(22)–Mo(3)–S(1)	102.2(1)
O(10)–Mo(1)–O(23)	167.4(2)	O(23)–Mo(3)–Mo(1)	48.2(1)
O(10)–Mo(1)–N(1)	86.1(2)	O(23)–Mo(3)–Mo(2)	92.1(1)
O(10)–Mo(1)–S(1)	90.0(1)	O(23)–Mo(3)–N(5)	80.4(2)
O(20)–Mo(1)–Mo(2)	144.6(1)	O(23)–Mo(3)–S(1)	104.2(1)
O(20)–Mo(1)–Mo(3)	96.1(1)	N(5)–Mo(3)–Mo(1)	128.5(1)
O(20)–Mo(1)–O(21)	168.4(2)	N(5)–Mo(3)–Mo(2)	132.8(1)
O(20)–Mo(1)–O(23)	88.8(2)	N(5)–Mo(3)–S(1)	170.0(1)
O(20)–Mo(1)–N(1)	82.8(2)	S(1)–Mo(3)–Mo(1)	56.99(3)
O(20)–Mo(1)–S(1)	88.5(1)	S(1)–Mo(3)–Mo(2)	56.59(3)
O(21)–Mo(1)–Mo(2)	47.0(1)	O(1)–Mo(4)–O(2)	72.4(2)
O(21)–Mo(1)–Mo(3)	91.4(1)	O(1)–Mo(4)–O(4)	76.0(1)
O(21)–Mo(1)–O(23)	89.8(2)	O(1)–Mo(4)–O(8)	94.4(2)
O(21)–Mo(1)–N(1)	85.6(2)	O(1)–Mo(4)–O(9)	155.3(2)
O(21)–Mo(1)–S(1)	103.1(1)	O(1)–Mo(4)–O(10)	89.8(2)
O(23)–Mo(1)–Mo(2)	92.0(1)	O(2)–Mo(4)–O(4)	78.1(2)
O(23)–Mo(1)–Mo(3)	46.9(1)	O(2)–Mo(4)–O(8)	93.8(2)
O(23)–Mo(1)–N(1)	81.4(2)	O(2)–Mo(4)–O(9)	90.4(2)
O(23)–Mo(1)–S(1)	102.7(1)	O(2)–Mo(4)–O(10)	156.5(2)
N(1)–Mo(1)–Mo(2)	132.3(1)	O(4)–Mo(4)–O(8)	168.9(2)

N(1)–Mo(1)–Mo(3)	128.3(1)	O(4)–Mo(4)–O(9)	83.4(2)
N(1)–Mo(1)–S(1)	170.3(1)	O(4)–Mo(4)–O(10)	82.9(2)
S(1)–Mo(1)–Mo(2)	56.86(3)	O(8)–Mo(4)–O(9)	104.4(2)
S(1)–Mo(1)–Mo(3)	56.73(3)	O(8)–Mo(4)–O(10)	103.0(2)
Mo(1)–Mo(2)–Mo(3)	59.83(2)	O(9)–Mo(4)–O(10)	101.0(2)
O(1)–Mo(2)–Mo(1)	92.0(1)	O(11)–Mo(5)–O(12)	72.8(1)
O(1)–Mo(2)–Mo(3)	141.3(1)	O(11)–Mo(5)–O(14)	77.5(2)
O(1)–Mo(2)–O(6)	82.4(2)	O(11)–Mo(5)–O(18)	90.5(2)
O(1)–Mo(2)–O(21)	86.6(2)	O(11)–Mo(5)–O(19)	157.1(2)
O(1)–Mo(2)–O(22)	170.7(2)	O(11)–Mo(5)–O(20)	90.8(2)
O(1)–Mo(2)–N(3)	85.0(2)	O(12)–Mo(5)–O(14)	77.7(2)
O(1)–Mo(2)–S(1)	86.5(1)	O(12)–Mo(5)–O(18)	90.5(2)
O(6)–Mo(2)–Mo(1)	145.3(1)	O(12)–Mo(5)–O(19)	88.9(2)
O(6)–Mo(2)–Mo(3)	105.4(1)	O(12)–Mo(5)–O(20)	158.9(2)
O(6)–Mo(2)–O(21)	162.1(2)	O(14)–Mo(5)–O(18)	165.1(2)
O(6)–Mo(2)–O(22)	93.7(2)	O(14)–Mo(5)–O(19)	85.2(2)
O(6)–Mo(2)–N(3)	83.0(2)	O(14)–Mo(5)–O(20)	85.9(2)
O(6)–Mo(2)–S(1)	88.4(1)	O(18)–Mo(5)–O(19)	103.8(2)
O(21)–Mo(2)–Mo(1)	48.7(1)	O(18)–Mo(5)–O(20)	103.2(2)
O(21)–Mo(2)–Mo(3)	92.0(1)	O(19)–Mo(5)–O(20)	103.0(2)
O(21)–Mo(2)–O(22)	95.1(2)	Mo(1)–O(21)–Mo(2)	84.3(1)
O(21)–Mo(2)–N(3)	82.1(2)	Mo(1)–S(1)–Mo(2)	66.11(4)
O(21)–Mo(2)–S(1)	104.9(1)	Mo(1)–O(23)–Mo(3)	84.9(2)
O(22)–Mo(2)–Mo(1)	96.0(1)	Mo(1)–S(1)–Mo(3)	66.29(4)
O(22)–Mo(2)–Mo(3)	47.9(1)	Mo(1)–O(10)–Mo(4)	134.0(2)
O(22)–Mo(2)–N(3)	86.2(2)	Mo(1)–O(20)–Mo(5)	132.9(2)
O(22)–Mo(2)–S(1)	101.9(1)	Mo(2)–O(22)–Mo(3)	83.9(2)
N(3)–Mo(2)–Mo(1)	130.7(1)	Mo(2)–S(1)–Mo(3)	66.90(4)
N(3)–Mo(2)–Mo(3)	133.2(1)	Mo(2)–O(1)–Mo(4)	120.8(2)
N(3)–Mo(2)–S(1)	168.6(1)	Mo(3)–O(11)–Mo(5)	121.3(2)
S(1)–Mo(2)–Mo(1)	57.04(3)	C(1)–O(1)–Mo(2)	122.8(3)
S(1)–Mo(2)–Mo(3)	56.51(3)	C(1)–O(1)–Mo(4)	113.1(3)
Mo(1)–Mo(3)–Mo(2)	59.64(2)	C(2)–O(2)–Mo(4)	118.6(4)
O(11)–Mo(3)–Mo(1)	91.9(1)	C(4)–O(4)–Mo(4)	134.8(4)
O(11)–Mo(3)–Mo(2)	141.1(1)	C(6)–O(6)–Mo(2)	131.7(4)
O(11)–Mo(3)–O(16)	83.0(2)	C(7)–O(11)–Mo(3)	123.4(3)
O(11)–Mo(3)–O(22)	170.7(2)	C(7)–O(11)–Mo(5)	112.7(3)
O(11)–Mo(3)–O(23)	85.6(2)	C(8)–O(12)–Mo(5)	121.3(4)
O(11)–Mo(3)–N(5)	85.2(2)	C(10)–O(14)–Mo(5)	137.0(4)
O(11)–Mo(3)–S(1)	86.3(1)	C(12)–O(16)–Mo(3)	132.0(4)
O(16)–Mo(3)–Mo(1)	145.9(1)	C(13)–N(1)–Mo(1)	126.7(4)
O(16)–Mo(3)–Mo(2)	105.4(1)	C(15)–N(1)–Mo(1)	126.5(4)
O(16)–Mo(3)–O(22)	93.1(2)	C(16)–N(3)–Mo(2)	127.9(4)
O(16)–Mo(3)–O(23)	162.1(2)	C(18)–N(3)–Mo(2)	126.0(4)

O(16)–Mo(3)–N(5)	84.8(2)	C(19)–N(5)–Mo(3)	122.3(4)
O(16)–Mo(3)–S(1)	88.9(1)	C(21)–N(5)–Mo(3)	131.8(4)

Table S9. Selected bond distances (Å) and angles (°) for *trans*-[$(Mo^{V}O)_2O(H_2homocit)_2(bpy)_2$] $4H_2O$ (**3**).

Mo(1)–O(1)	1.949 (1)	Mo(2)–O(9)	1.873(1)
Mo(1)–O(2)	2.065(2)	Mo(2)–O(10)	1.954(1)
Mo(1)–O(8)	1.671(1)	Mo(2)–O(11)	2.070 (1)
Mo(1)–O(9)	1.861(1)	Mo(2)–O(17)	1.669(1)
Mo(1)–N(1)	2.222(2)	Mo(2)–N(3)	2.309(1)
Mo(1)–N(2)	2.324(2)	Mo(2)–N(4)	2.237(2)
O(1)–Mo(1)–O(2)	78.80(6)	O(11)–Mo(2)–N(3)	83.39(5)
O(1)–Mo(1)–N(1)	160.10(6)	O(11)–Mo(2)–N(4)	87.89(5)
O(1)–Mo(1)–N(2)	91.70(5)	O(17)–Mo(2)–O(9)	101.19(6)
O(2)–Mo(1)–N(1)	89.99(6)	O(17)–Mo(2)–O(10)	109.74(6)
O(2)–Mo(1)–N(2)	81.25(5)	O(17)–Mo(2)–O(11)	97.77(6)
O(8)–Mo(1)–O(1)	109.86(6)	O(17)–Mo(2)–N(3)	156.21(7)
O(8)–Mo(1)–O(2)	98.22(6)	O(17)–Mo(2)–N(4)	85.97(6)
O(8)–Mo(1)–O(9)	102.04(6)	N(3)–Mo(2)–N(4)	70.30(5)
O(8)–Mo(1)–N(1)	87.83(6)	Mo(1)–O(9)–Mo(2)	168.00(7)
O(8)–Mo(1)–N(2)	158.00(6)	C(1)–O(1)–Mo(1)	118.9(1)
O(9)–Mo(1)–O(1)	92.51(5)	C(2)–O(2)–Mo(1)	116.1(2)
O(9)–Mo(1)–O(2)	159.66(5)	C(8)–N(1)–Mo(1)	119.7(1)
O(9)–Mo(1)–N(1)	92.56(5)	C(12)–N(1)–Mo(1)	121.0(1)
O(9)–Mo(1)–N(2)	80.66(5)	C(13)–N(2)–Mo(1)	118.4(1)
N(1)–Mo(1)–N(2)	70.20(5)	C(17)–N(2)–Mo(1)	121.8(1)
O(9)–Mo(2)–O(10)	91.88(5)	C(18)–O(10)–Mo(2)	116.2(1)
O(9)–Mo(2)–O(11)	160.74(5)	C(19)–O(11)–Mo(2)	115.9(1)
O(9)–Mo(2)–N(3)	80.64(5)	C(25)–N(3)–Mo(2)	122.2(1)
O(9)–Mo(2)–N(4)	96.74(5)	C(29)–N(3)–Mo(2)	118.5(1)
O(10)–Mo(2)–O(11)	78.48(5)	C(30)–N(4)–Mo(2)	121.4(1)
O(10)–Mo(2)–N(3)	93.82(5)	C(34)–N(4)–Mo(2)	120.7(1)
O(10)–Mo(2)–N(4)	160.29(6)		

Table S10. Selected bond distances (Å) and angles (°) for $(Et_4N)[Mo^{VI}O_2Cl(H_2cit)]\cdot H_2O$ (**4**).

Mo(1)–Cl(1)	2.358(2)	Mo(1)–O(4)	2.433(4)
Mo(1)–O(1)	1.931(4)	Mo(1)–O(8)	1.701(4)
Mo(1)–O(2)	2.178(3)	Mo(1)–O(9)	1.690(4)
O(1)–Mo(1)–O(2)	76.0(2)	O(9)–Mo(1)–O(1)	103.1(2)
O(1)–Mo(1)–O(4)	76.2(2)	O(9)–Mo(1)–O(2)	95.7(2)
O(1)–Mo(1)–Cl(1)	150.1(1)	O(9)–Mo(1)–O(4)	172.1(2)
O(2)–Mo(1)–O(4)	76.5(1)	O(9)–Mo(1)–O(8)	103.3(2)
O(2)–Mo(1)–Cl(1)	81.1(1)	O(9)–Mo(1)–Cl(1)	98.1(2)
O(8)–Mo(1)–O(1)	99.0(2)	Cl(1)–Mo(1)–O(4)	80.0(1)
O(8)–Mo(1)–O(2)	161.0(2)	C(1)–O(1)–Mo(1)	119.9(3)
O(8)–Mo(1)–O(4)	84.5(2)	C(2)–O(2)–Mo(1)	114.8(3)
O(8)–Mo(1)–Cl(1)	96.5(2)	C(4)–O(4)–Mo(1)	124.8(4)

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