

Electronic Supplementary Information (ESI)

Synthesis, structures and theoretical investigation of three polyoxomolybdate-based compounds: self-assembling, fragment analysis, orbital interaction, and formation mechanism

Table S1. Crystallographic Data and Structure Refinement Parameters for Compounds 1–3

	1	2	3
formula	C ₁₆ H ₂₄ CuMo ₄ N ₈ O ₁₃	C ₅₄ H ₅₉ Mo ₁₂ N ₂₇ O ₄₅ Si	C ₂₄ H ₂₈ Mo ₁₂ N ₁₂ O ₄₂ Si
<i>F</i> w	983.73	2985.65	2335.95
crystal system	monoclinic	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>m</i>	<i>P</i> -1
<i>a</i> (Å)	13.1126(15)	23.3171(13)	11.6044(4)
<i>b</i> (Å)	16.1764(19)	15.7546(9)	13.1169(4)
<i>c</i> (Å)	17.1279(15)	12.0657(7)	20.4496(9)
α (°)	90	90	99.347(2)
β (°)	123.896(6)	94.9490(10)	93.793(2)
γ (°)	90	90	113.837(2)
<i>V</i> (Å ³)	3015.6(6)	4415.8(4)	1258.99(2)
<i>Z</i>	4	2	2
<i>D</i> _c (g·cm ⁻³)	2.167	2.245	2.791
μ (mm ⁻¹)	2.382	1.765	2.749
<i>F</i> (000)	1908	2900	2220
reflns collected/unique	15868/4529	16040/5149	53969/14351
GOF on <i>F</i> ²	1.003	1.061	1.037
final <i>R</i> ₁ ^a , <i>wR</i> ₂ ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0573, 0.1219	0.0514, 0.1396	0.0382, 0.0742
final <i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (all data)	0.1062, 0.1441	0.0632, 0.1479	0.0599, 0.0825
$\Delta\rho_{max}/\Delta\rho_{min}$ (e·Å ⁻³)	2.047/-1.090	1.859/-0.638	1.282/-2.120

^a $R_1 = \sum \| |F_o| - |F_c| \| / \sum |F_o|$. ^b $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$.

Table S2. Selected Bond Lengths (Å) and Bond Angles (°) for Compounds 1–3

1					
Cu(1)-N(7)	2.005(9)	Mo(1)-O(11)	2.492(8)	Mo(3)-O(10)#1	2.359(8)
Cu(1)-N(11)	2.007(9)	Mo(4)-O(13)	1.690(8)	Mo(3)-O(2)	2.407(8)
Cu(1)-N(5)	2.011(10)	Mo(4)-O(11)	1.776(7)	Mo(2)-O(1)	1.689(7)
Cu(1)-N(9)	2.024(9)	Mo(4)-O(10)	1.800(8)	Mo(2)-O(6)	1.699(7)
Mo(1)-O(9)	1.672(9)	Mo(4)-O(2)	1.802(7)	Mo(2)-O(3)	1.904(7)
Mo(1)-O(12)	1.702(8)	Mo(3)-O(5)	1.685(7)	Mo(2)-O(4)	1.917(7)
Mo(1)-O(7)	1.883(7)	Mo(3)-O(8)	1.700(8)	Mo(2)-O(11)	2.365(7)
Mo(1)-O(4)	1.894(7)	Mo(3)-O(3)	1.900(7)	Mo(2)-O(10)#1	2.398(7)
Mo(1)-O(2)#1	2.474(8)	Mo(3)-O(7)#1	1.922(7)		
N(7)-Cu(1)-N(11)	92.3(4)	O(4)-Mo(1)-O(11)	70.4(3)	O(8)-Mo(3)-O(2)	163.6(3)
N(7)-Cu(1)-N(5)	176.0(4)	O(2)#1-Mo(1)-O(11)	76.3(2)	O(3)-Mo(3)-O(2)	79.9(3)
N(11)-Cu(1)-N(5)	87.7(4)	O(13)-Mo(4)-O(11)	109.1(4)	O(7)#1-Mo(3)-O(2)	71.9(3)
N(7)-Cu(1)-N(9)	87.7(4)	O(13)-Mo(4)-O(10)	110.1(4)	O(10)#1-Mo(3)-O(2)	77.5(3)
N(11)-Cu(1)-N(9)	175.5(4)	O(11)-Mo(4)-O(10)	109.2(3)	O(1)-Mo(2)-O(6)	105.6(4)
N(5)-Cu(1)-N(9)	92.7(4)	O(13)-Mo(4)-O(2)	109.0(4)	O(1)-Mo(2)-O(3)	100.0(3)
O(9)-Mo(1)-O(12)	105.8(4)	O(11)-Mo(4)-O(2)	110.0(3)	O(6)-Mo(2)-O(3)	101.0(3)
O(9)-Mo(1)-O(7)	100.0(4)	O(10)-Mo(4)-O(2)	109.5(4)	O(1)-Mo(2)-O(4)	102.5(3)
O(12)-Mo(1)-O(7)	103.9(4)	O(5)-Mo(3)-O(8)	105.4(4)	O(6)-Mo(2)-O(4)	98.4(3)
O(9)-Mo(1)-O(4)	103.5(4)	O(5)-Mo(3)-O(3)	98.0(3)	O(3)-Mo(2)-O(4)	144.9(3)
O(12)-Mo(1)-O(4)	100.1(3)	O(8)-Mo(3)-O(3)	103.4(3)	O(1)-Mo(2)-O(11)	88.7(3)
O(7)-Mo(1)-O(4)	140.2(3)	O(5)-Mo(3)-O(7)#1	101.7(3)	O(6)-Mo(2)-O(11)	164.8(3)
O(9)-Mo(1)-O(2)#1	165.7(4)	O(8)-Mo(3)-O(7)#1	98.5(3)	O(3)-Mo(2)-O(11)	81.0(3)
O(12)-Mo(1)-O(2)#1	87.5(3)	O(3)-Mo(3)-O(7)#1	145.3(3)	O(4)-Mo(2)-O(11)	73.0(3)
O(7)-Mo(1)-O(2)#1	70.9(3)	O(5)-Mo(3)-O(10)#1	165.2(3)	O(1)-Mo(2)-O(10)#1	162.9(3)
O(4)-Mo(1)-O(2)#1	78.9(3)	O(8)-Mo(3)-O(10)#1	88.2(3)	O(6)-Mo(2)-O(10)#1	90.8(3)
O(9)-Mo(1)-O(11)	91.1(4)	O(3)-Mo(3)-O(10)#1	72.6(3)	O(3)-Mo(2)-O(10)#1	71.6(3)
O(12)-Mo(1)-O(11)	162.4(3)	O(7)#1-Mo(3)- O(10)#1	81.6(3)	O(4)-Mo(2)-O(10)#1	79.2(3)
O(7)-Mo(1)-O(11)	77.5(3)	O(5)-Mo(3)-O(2)	89.8(3)	O(11)-Mo(2)-O(10)#1	75.5(3)
2					
Mo(1)-O(4)	1.652(12)	Mo(2)-O(6)	2.378(12)	Mo(4)-O(8)#2	1.997(11)
Mo(1)-O(7)#2	1.805(11)	Mo(2)-O(10)	2.418(13)	Mo(4)-O(8)	1.997(11)
Mo(1)-O(7)	1.805(11)	Mo(3)-O(1)	1.662(9)	Mo(4)-O(6)#2	2.418(12)
Mo(1)-O(9)	1.984(11)	Mo(3)-O(5)	1.793(11)	Mo(4)-O(6)	2.418(12)
Mo(1)-O(9)#2	1.984(11)	Mo(3)-O(11)	1.818(10)	Si(1)-O(10)#3	1.604(12)
Mo(1)-O(10)#2	2.393(12)	Mo(3)-O(12)#3	1.983(11)	Si(1)-O(10)#4	1.604(12)
Mo(1)-O(10)	2.393(12)	Mo(3)-O(7)	2.006(11)	Si(1)-O(10)#2	1.604(12)
Mo(2)-O(3)	1.643(9)	Mo(3)-O(6)#3	2.361(12)	Si(1)-O(10)	1.604(12)
Mo(2)-O(8)	1.785(11)	Mo(3)-O(10)	2.410(13)	Si(1)-O(6)#4	1.641(12)

Mo(2)-O(9)	1.807(11)	Mo(4)-O(2)	1.659(13)	Si(1)-O(6)#3	1.641(12)
Mo(2)-O(11)#3	1.996(10)	Mo(4)-O(12)#2	1.816(11)	Si(1)-O(6)	1.641(12)
Mo(2)-O(5)	2.021(11)	Mo(4)-O(12)	1.816(11)	Si(1)-O(6)#2	1.641(12)
O(4)-Mo(1)-O(7)#2	101.7(5)	O(9)-Mo(2)-O(10)	64.5(5)	O(8)#2-Mo(4)-O(6)#2	62.0(4)
O(4)-Mo(1)-O(7)	101.7(5)	O(11)#3-Mo(2)-O(10)	92.1(4)	O(8)-Mo(4)-O(6)#2	92.2(4)
O(7)#2-Mo(1)-O(7)	96.4(7)	O(5)-Mo(2)-O(10)	62.6(4)	O(2)-Mo(4)-O(6)	155.7(3)
O(4)-Mo(1)-O(9)	99.5(5)	O(6)-Mo(2)-O(10)	46.0(4)	O(12)#2-Mo(4)-O(6)	99.3(5)
O(7)#2-Mo(1)-O(9)	156.9(5)	O(1)-Mo(3)-O(5)	101.1(5)	O(12)-Mo(4)-O(6)	63.9(4)
O(7)-Mo(1)-O(9)	88.1(5)	O(1)-Mo(3)-O(11)	103.0(5)	O(8)#2-Mo(4)-O(6)	92.2(4)
O(4)-Mo(1)-O(9)#2	99.5(5)	O(5)-Mo(3)-O(11)	97.7(5)	O(8)-Mo(4)-O(6)	62.0(4)
O(7)#2-Mo(1)-O(9)#2	88.1(5)	O(1)-Mo(3)-O(12)#3	98.6(5)	O(6)#2-Mo(4)-O(6)	47.2(6)
O(7)-Mo(1)-O(9)#2	156.9(5)	O(5)-Mo(3)-O(12)#3	157.7(5)	O(10)#3-Si(1)- O(10)#4	68.4(9)
O(9)-Mo(1)-O(9)#2	79.5(7)	O(11)-Mo(3)-O(12)#3	87.9(5)	O(10)#3-Si(1)- O(10)#2	180.0(10)
O(4)-Mo(1)-O(10)#2	157.3(3)	O(1)-Mo(3)-O(7)	97.3(5)	O(10)#4-Si(1)- O(10)#2	111.6(9)
O(7)#2-Mo(1)- O(10)#2	65.4(5)	O(5)-Mo(3)-O(7)	87.6(5)	O(10)#3-Si(1)-O(10)	111.6(9)
O(7)-Mo(1)-O(10)#2	98.3(5)	O(11)-Mo(3)-O(7)	157.6(5)	O(10)#4-Si(1)-O(10)	180.0(7)
O(9)-Mo(1)-O(10)#2	91.6(4)	O(12)#3-Mo(3)-O(7)	79.6(4)	O(10)#2-Si(1)-O(10)	68.4(9)
O(9)#2-Mo(1)- O(10)#2	63.0(4)	O(1)-Mo(3)-O(6)#3	156.9(5)	O(10)#3-Si(1)-O(6)#4	109.3(6)
O(4)-Mo(1)-O(10)	157.3(3)	O(5)-Mo(3)-O(6)#3	99.8(4)	O(10)#4-Si(1)-O(6)#4	70.6(6)
O(7)#2-Mo(1)-O(10)	98.3(5)	O(11)-Mo(3)-O(6)#3	64.5(5)	O(10)#2-Si(1)-O(6)#4	70.7(6)
O(7)-Mo(1)-O(10)	65.4(5)	O(12)#3-Mo(3)- O(6)#3	63.1(4)	O(10)-Si(1)-O(6)#4	109.4(6)
O(9)-Mo(1)-O(10)	63.0(4)	O(7)-Mo(3)-O(6)#3	93.2(4)	O(10)#3-Si(1)-O(6)#3	70.6(6)
O(9)#2-Mo(1)-O(10)	91.6(4)	O(1)-Mo(3)-O(10)	155.1(5)	O(10)#4-Si(1)-O(6)#3	109.3(6)
O(10)#2-Mo(1)-O(10)	44.3(6)	O(5)-Mo(3)-O(10)	65.5(5)	O(10)#2-Si(1)-O(6)#3	109.4(6)
O(3)-Mo(2)-O(8)	103.7(5)	O(11)-Mo(3)-O(10)	99.8(5)	O(10)-Si(1)-O(6)#3	70.7(6)
O(3)-Mo(2)-O(9)	102.7(5)	O(12)#3-Mo(3)-O(10)	92.3(4)	O(6)#4-Si(1)-O(6)#3	72.2(8)
O(8)-Mo(2)-O(9)	98.2(5)	O(7)-Mo(3)-O(10)	62.6(4)	O(10)#3-Si(1)-O(6)	70.7(6)
O(3)-Mo(2)-O(11)#3	97.7(5)	O(6)#3-Mo(3)-O(10)	46.4(4)	O(10)#4-Si(1)-O(6)	109.4(6)
O(8)-Mo(2)-O(11)#3	88.4(5)	O(2)-Mo(4)-O(12)#2	102.5(4)	O(10)#2-Si(1)-O(6)	109.3(6)
O(9)-Mo(2)-O(11)#3	156.4(5)	O(2)-Mo(4)-O(12)	102.5(4)	O(10)-Si(1)-O(6)	70.6(6)
O(3)-Mo(2)-O(5)	97.3(5)	O(12)#2-Mo(4)-O(12)	97.5(7)	O(6)#4-Si(1)-O(6)	180.0(7)
O(8)-Mo(2)-O(5)	156.7(5)	O(2)-Mo(4)-O(8)#2	99.2(4)	O(6)#3-Si(1)-O(6)	107.8(8)
O(9)-Mo(2)-O(5)	86.9(5)	O(12)#2-Mo(4)- O(8)#2	87.5(5)	O(10)#3-Si(1)-O(6)#2	109.4(6)
O(11)#3-Mo(2)-O(5)	78.7(4)	O(12)-Mo(4)-O(8)#2	156.0(5)	O(10)#4-Si(1)-O(6)#2	70.7(6)
O(3)-Mo(2)-O(6)	155.9(5)	O(2)-Mo(4)-O(8)	99.2(4)	O(10)#2-Si(1)-O(6)#2	70.6(6)
O(8)-Mo(2)-O(6)	65.3(5)	O(12)#2-Mo(4)-O(8)	156.0(5)	O(10)-Si(1)-O(6)#2	109.3(6)

O(9)-Mo(2)-O(6)	100.2(5)	O(12)-Mo(4)-O(8)	87.5(5)	O(6)#4-Si(1)-O(6)#2	107.8(8)
O(11)#3-Mo(2)-O(6)	62.0(4)	O(8)#2-Mo(4)-O(8)	79.0(6)	O(6)#3-Si(1)-O(6)#2	180.0(9)
O(5)-Mo(2)-O(6)	91.4(4)	O(2)-Mo(4)-O(6)#2	155.7(3)	O(6)-Si(1)-O(6)#2	72.2(8)
O(3)-Mo(2)-O(10)	155.5(5)	O(12)#2-Mo(4)- O(6)#2	63.9(4)		
O(8)-Mo(2)-O(10)	99.0(5)	O(12)-Mo(4)-O(6)#2	99.3(5)		

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Mo(1)-O(15)	1.677(3)	Mo(5)-O(10)	1.866(3)	Mo(9)-O(38)	1.958(3)
Mo(1)-O(3)	1.894(3)	Mo(5)-O(23)	1.972(3)	Mo(9)-O(20)	2.361(3)
Mo(1)-O(29)	1.902(3)	Mo(5)-O(18)	1.991(3)	Mo(10)-O(24)	1.676(3)
Mo(1)-O(9)	1.940(3)	Mo(5)-O(1)	2.340(3)	Mo(10)-O(18)	1.832(3)
Mo(1)-O(2)	1.955(3)	Mo(6)-O(37)	1.691(3)	Mo(10)-O(27)	1.930(3)
Mo(1)-O(13)	2.352(3)	Mo(6)-O(2)	1.862(3)	Mo(10)-O(16)	1.954(3)
Mo(2)-O(8)	1.676(3)	Mo(6)-O(40)	1.868(3)	Mo(10)-O(28)	2.000(3)
Mo(2)-O(34)	1.885(3)	Mo(6)-O(10)	1.961(3)	Mo(10)-O(20)	2.322(3)
Mo(2)-O(23)	1.899(3)	Mo(6)-O(34)	1.980(3)	Mo(11)-O(21)	1.695(3)
Mo(2)-O(26)	1.949(3)	Mo(6)-O(1)	2.341(3)	Mo(11)-O(17)	1.838(3)
Mo(2)-O(19)	1.954(3)	Mo(7)-O(32)	1.683(3)	Mo(11)-O(36)	1.883(3)
Mo(2)-O(1)	2.353(3)	Mo(7)-O(7)	1.898(3)	Mo(11)-O(35)	1.967(3)
Mo(3)-O(5)	1.677(3)	Mo(7)-O(33)	1.916(3)	Mo(11)-O(7)	1.987(3)
Mo(3)-O(25)	1.852(3)	Mo(7)-O(27)	1.916(3)	Mo(11)-O(4)	2.321(3)
Mo(3)-O(22)	1.869(3)	Mo(7)-O(11)	1.957(3)	Mo(12)-O(30)	1.688(3)
Mo(3)-O(17)	1.979(3)	Mo(7)-O(4)	2.345(3)	Mo(12)-O(28)	1.872(3)
Mo(3)-O(3)	1.997(3)	Mo(8)-O(39)	1.672(3)	Mo(12)-O(38)	1.893(3)
Mo(3)-O(13)	2.337(3)	Mo(8)-O(9)	1.899(3)	Mo(12)-O(25)	1.961(3)
Mo(4)-O(14)	1.690(3)	Mo(8)-O(35)	1.901(3)	Mo(12)-O(36)	1.963(3)
Mo(4)-O(19)	1.864(3)	Mo(8)-O(33)	1.936(3)	Mo(12)-O(20)	2.363(3)
Mo(4)-O(6)	1.890(3)	Mo(8)-O(40)	1.959(3)	Si(1)-O(13)	1.623(3)
Mo(4)-O(29)	1.948(3)	Mo(8)-O(4)	2.363(3)	Si(1)-O(1)	1.627(3)
Mo(4)-O(22)	1.976(3)	Mo(9)-O(31)	1.680(3)	Si(1)-O(20)	1.628(3)
Mo(4)-O(13)	2.348(3)	Mo(9)-O(26)	1.878(3)	Si(1)-O(4)	1.630(3)
Mo(5)-O(12)	1.675(3)	Mo(9)-O(6)	1.928(3)		
Mo(5)-O(11)	1.861(3)	Mo(9)-O(16)	1.933(3)		

O(15)-Mo(1)-O(3)	101.83(14))	O(11)-Mo(5)-O(10)	94.99(13)	O(26)-Mo(9)-O(16)	90.47(13)
O(15)-Mo(1)-O(29)	100.57(14))	O(12)-Mo(5)-O(23)	98.91(14)	O(6)-Mo(9)-O(16)	158.72(12))
O(3)-Mo(1)-O(29)	91.12(13)	O(11)-Mo(5)-O(23)	156.90(12))	O(31)-Mo(9)-O(38)	100.26(16))
O(15)-Mo(1)-O(9)	100.13(14))	O(10)-Mo(5)-O(23)	89.15(13)	O(26)-Mo(9)-O(38)	157.77(13))
O(3)-Mo(1)-O(9)	89.02(12)	O(12)-Mo(5)-O(18)	99.37(14)	O(6)-Mo(9)-O(38)	87.77(13)
O(29)-Mo(1)-O(9)	158.81(12)	O(11)-Mo(5)-O(18)	84.59(13)	O(16)-Mo(9)-O(38)	86.92(13)

O(15)-Mo(1)-O(2)	99.28(14)	O(10)-Mo(5)-O(18)	158.93(12)	O(31)-Mo(9)-O(20)	170.67(14)
O(3)-Mo(1)-O(2)	158.62(12)	O(23)-Mo(5)-O(18)	83.51(13)	O(26)-Mo(9)-O(20)	84.63(11)
O(29)-Mo(1)-O(2)	88.31(13)	O(12)-Mo(5)-O(1)	171.48(12)	O(6)-Mo(9)-O(20)	84.86(11)
O(9)-Mo(1)-O(2)	83.96(12)	O(11)-Mo(5)-O(1)	85.64(11)	O(16)-Mo(9)-O(20)	73.87(11)
O(15)-Mo(1)-O(13)	173.72(13)	O(10)-Mo(5)-O(1)	75.29(11)	O(38)-Mo(9)-O(20)	73.43(12)
O(3)-Mo(1)-O(13)	74.87(11)	O(23)-Mo(5)-O(1)	73.43(11)	O(24)-Mo(10)-O(18)	104.43(15)
O(29)-Mo(1)-O(13)	74.35(11)	O(18)-Mo(5)-O(1)	83.68(11)	O(24)-Mo(10)-O(27)	101.18(14)
O(9)-Mo(1)-O(13)	85.26(11)	O(37)-Mo(6)-O(2)	102.22(15)	O(18)-Mo(10)-O(27)	88.63(13)
O(2)-Mo(1)-O(13)	84.42(11)	O(37)-Mo(6)-O(40)	103.46(16)	O(24)-Mo(10)-O(16)	97.68(14)
O(8)-Mo(2)-O(34)	100.85(16)	O(2)-Mo(6)-O(40)	89.52(13)	O(18)-Mo(10)-O(16)	91.88(13)
O(8)-Mo(2)-O(23)	99.96(15)	O(37)-Mo(6)-O(10)	98.78(15)	O(27)-Mo(10)-O(16)	160.39(12)
O(34)-Mo(2)-O(23)	91.32(13)	O(2)-Mo(6)-O(10)	158.67(13)	O(24)-Mo(10)-O(28)	96.62(15)
O(8)-Mo(2)-O(26)	100.02(16)	O(40)-Mo(6)-O(10)	89.17(13)	O(18)-Mo(10)-O(28)	158.91(13)
O(34)-Mo(2)-O(26)	158.82(13)	O(37)-Mo(6)-O(34)	97.67(16)	O(27)-Mo(10)-O(28)	86.13(13)
O(23)-Mo(2)-O(26)	88.58(13)	O(2)-Mo(6)-O(34)	88.45(13)	O(16)-Mo(10)-O(28)	86.40(13)
O(8)-Mo(2)-O(19)	101.16(15)	O(40)-Mo(6)-O(34)	158.71(13)	O(24)-Mo(10)-O(20)	167.14(14)
O(34)-Mo(2)-O(19)	89.33(13)	O(10)-Mo(6)-O(34)	85.11(12)	O(18)-Mo(10)-O(20)	86.22(12)
O(23)-Mo(2)-O(19)	158.36(12)	O(37)-Mo(6)-O(1)	168.37(14)	O(27)-Mo(10)-O(20)	86.04(11)
O(26)-Mo(2)-O(19)	83.15(13)	O(2)-Mo(6)-O(1)	85.02(12)	O(16)-Mo(10)-O(20)	74.44(11)
O(8)-Mo(2)-O(1)	172.38(14)	O(40)-Mo(6)-O(1)	85.51(12)	O(28)-Mo(10)-O(20)	73.05(11)
O(34)-Mo(2)-O(1)	74.53(11)	O(10)-Mo(6)-O(1)	73.66(11)	O(21)-Mo(11)-O(17)	101.90(14)
O(23)-Mo(2)-O(1)	74.36(11)	O(34)-Mo(6)-O(1)	73.21(11)	O(21)-Mo(11)-O(36)	102.08(16)
O(26)-Mo(2)-O(1)	85.08(11)	O(32)-Mo(7)-O(7)	101.19(14)	O(17)-Mo(11)-O(36)	89.29(13)
O(19)-Mo(2)-O(1)	85.00(11)	O(32)-Mo(7)-O(33)	100.72(15)	O(21)-Mo(11)-O(35)	97.47(15)

)		
O(5)-Mo(3)-O(25)	103.44(15)	O(7)-Mo(7)-O(33)	89.83(13)	O(17)-Mo(11)-O(35)	90.53(13)
)				
O(5)-Mo(3)-O(22)	101.16(14)	O(32)-Mo(7)-O(27)	99.62(15)	O(36)-Mo(11)-O(35)	160.06(13)
))
O(25)-Mo(3)-O(22)	95.04(13)	O(7)-Mo(7)-O(27)	91.17(13)	O(21)-Mo(11)-O(7)	97.99(14)
O(5)-Mo(3)-O(17)	99.35(14)	O(33)-Mo(7)-O(27)	159.04(12)	O(17)-Mo(11)-O(7)	160.03(12)
))
O(25)-Mo(3)-O(17)	86.08(12)	O(32)-Mo(7)-O(11)	100.74(14)	O(36)-Mo(11)-O(7)	88.31(12)
)		
O(22)-Mo(3)-O(17)	158.59(13)	O(7)-Mo(7)-O(11)	158.05(12)	O(35)-Mo(11)-O(7)	85.09(13)
))		
O(5)-Mo(3)-O(3)	97.31(14)	O(33)-Mo(7)-O(11)	87.08(13)	O(21)-Mo(11)-O(4)	168.56(13)
)
O(25)-Mo(3)-O(3)	157.88(13)	O(27)-Mo(7)-O(11)	84.20(13)	O(17)-Mo(11)-O(4)	86.29(11)
)				
O(22)-Mo(3)-O(3)	88.33(13)	O(32)-Mo(7)-O(4)	173.47(13)	O(36)-Mo(11)-O(4)	85.83(12)
)		
O(17)-Mo(3)-O(3)	83.03(12)	O(7)-Mo(7)-O(4)	74.71(11)	O(35)-Mo(11)-O(4)	74.26(11)
O(5)-Mo(3)-O(13)	170.03(13)	O(33)-Mo(7)-O(4)	74.43(11)	O(7)-Mo(11)-O(4)	73.76(10)
)				
O(25)-Mo(3)-O(13)	86.22(12)	O(27)-Mo(7)-O(4)	85.65(11)	O(30)-Mo(12)-O(28)	101.18(16)
)
O(22)-Mo(3)-O(13)	75.16(11)	O(11)-Mo(7)-O(4)	83.54(11)	O(30)-Mo(12)-O(38)	100.99(17)
)
O(17)-Mo(3)-O(13)	83.59(11)	O(39)-Mo(8)-O(9)	102.30(15)	O(28)-Mo(12)-O(38)	91.00(14)
)		
O(3)-Mo(3)-O(13)	73.49(11)	O(39)-Mo(8)-O(35)	100.36(16)	O(30)-Mo(12)-O(25)	100.89(15)
))
O(14)-Mo(4)-O(19)	102.60(14)	O(9)-Mo(8)-O(35)	90.95(13)	O(28)-Mo(12)-O(25)	157.52(13)
))
O(14)-Mo(4)-O(6)	102.46(14)	O(39)-Mo(8)-O(33)	99.68(15)	O(38)-Mo(12)-O(25)	88.91(13)
)				
O(19)-Mo(4)-O(6)	88.80(13)	O(9)-Mo(8)-O(33)	157.72(13)	O(30)-Mo(12)-O(36)	100.28(17)
))
O(14)-Mo(4)-O(29)	99.06(14)	O(35)-Mo(8)-O(33)	88.66(13)	O(28)-Mo(12)-O(36)	89.62(13)
O(19)-Mo(4)-O(29)	90.20(13)	O(39)-Mo(8)-O(40)	100.13(16)	O(38)-Mo(12)-O(36)	158.18(13)
))
O(6)-Mo(4)-O(29)	158.15(12)	O(9)-Mo(8)-O(40)	84.57(13)	O(25)-Mo(12)-O(36)	82.34(12)
)				
O(14)-Mo(4)-O(22)	97.93(13)	O(35)-Mo(8)-O(40)	159.50(13)	O(30)-Mo(12)-O(20)	173.29(14)
))
O(19)-Mo(4)-O(22)	159.42(12)	O(33)-Mo(8)-O(40)	88.04(13)	O(28)-Mo(12)-O(20)	74.23(11)
)				

O(6)-Mo(4)-O(22)	88.26(13)	O(39)-Mo(8)-O(4)	171.39(13)	O(38)-Mo(12)-O(20)	74.47(12)
O(29)-Mo(4)-O(22)	85.05(13)	O(9)-Mo(8)-O(4)	84.77(11)	O(25)-Mo(12)-O(20)	84.12(11)
O(14)-Mo(4)-O(13)	168.65(12)	O(35)-Mo(8)-O(4)	74.38(11)	O(36)-Mo(12)-O(20)	84.73(11)
O(19)-Mo(4)-O(13)	86.37(11)	O(33)-Mo(8)-O(4)	73.67(11)	O(13)-Si(1)-O(1)	108.99(15)
O(6)-Mo(4)-O(13)	84.48(11)	O(40)-Mo(8)-O(4)	85.29(11)	O(13)-Si(1)-O(20)	109.43(15)
O(29)-Mo(4)-O(13)	73.67(10)	O(31)-Mo(9)-O(26)	101.94(16)	O(1)-Si(1)-O(20)	109.70(15)
O(22)-Mo(4)-O(13)	73.07(10)	O(31)-Mo(9)-O(6)	101.98(15)	O(13)-Si(1)-O(4)	109.85(14)
O(12)-Mo(5)-O(11)	102.52(14)	O(26)-Mo(9)-O(6)	86.71(13)	O(1)-Si(1)-O(4)	109.60(15)
O(12)-Mo(5)-O(10)	101.26(15)	O(31)-Mo(9)-O(16)	99.24(15)	O(20)-Si(1)-O(4)	109.26(15)

^a Symmetry transformations used to generate equivalent atoms. For **1**: #1, 1 - x, -y + 1, 1 - z; For **2**: #1, x, -y, z; #2, x, -y + 1, z; #3, -x + 1, y, -z + 1; #4, -x + 1, -y + 1, -z + 1; #5, x, -y + 2, z.

Table S3 The hydrogen bonding linkages in **2** and **3**

D-H...A	H...A	D...A	D-H...A
2			
O2W- H2W2... N1	2.012(17)	2.750(15)	144.8(16)
O2W- H2W1... O7	2.179(12)	3.009(11)	165.3(11)
N4- H4A... N3	1.85	2.69(2)	165.2
N1- H1A... O2W	1.91	2.750(15)	164.7
N22- H22... O11	1.78	2.629(12)	167.3
N22'- H22'... O3	2.22	2.879(10)	133.3
N22'- H22'... O11	1.97	2.724(12)	144.9
3			
O2W- H2W1... O28	2.05(5)	2.813(6)	148(8)
O1W- H1W2... O2	2.19(5)	2.963(6)	151(8)
N12- H12... O21	2.04	2.849(5)	156.2
N10- H10... O1W	1.84	2.699(7)	174.6
N9- H9A... O7	1.99	2.799(5)	157.4
N7- H7A... O17	2.65	3.085(5)	112.3
N7- H7A... O9	2.56	3.112(5)	122.6
N7- H7A... O3	2.02	2.866(5)	166.5
N6- H6A... O23	1.94	2.784(6)	167.9
N4- H4... O2W	1.84	2.672(7)	162.6
N3- H3... O16	1.93	2.724(5)	152.6
N1- H1... O27	2.62	3.217(5)	127.5
N1- H1... O32	2.55	3.270(5)	142
N1- H1... O14	2.25	2.856(5)	127.1