Supporting Information

A new polyoxometalate-templated Mo/V-oxide-based organic–inorganic hybrid framework with a honeycomb-like structure

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Experimental section

Materials and general methods. All chemicals were commercially purchased and used as supplied. Elemental analyses (P, V and Mo) were analyzed on a PLASMA-SPEC (I) ICP atomic emission spectrometer. The IR spectrum was recorded in the range 4000-400cm^{-1} on a TENSOR27 Bruker AXS spectrometer with a pressed KBr pellet. The TG-DTA analysis was carried out on a Pyris Diamond TG/DTA instrument in flowing N_2 with a heating rate of 10 ^{o}C·min^{-1}. Crystal data were collected on a SMART APEX II-CCD single crystal X-ray diffractometer with graphite-monochromated Mo Kα radiation (λ=0.71073 Å) at 293 K**.** The modified carbon paste electrodes of **1** (**1**-CPE) was fabricated as fellows: 0.5 g graphite powder (were purchased from Shanghai Chemical Plant and used as received) and 30 mg **1** were mixed and ground together with an agate mortar and pestle to achieve a uniform and dry mixture. To the mixture, 0.3 ml of paraffine was added and stirred with a glass rod, then the homogenized mixture was used to pack 3 mm inter diameter quartz tubes. The surface was wiped with weighing paper; electrical contact was established with copper rod through the back of the electrode. All electrochemical measurements were carried out on a CHI 600B electrochemical workstation at room temperature under nitrogen atmosphere. The working electrode was the **1**-CPE. A platinum wire was used as the counter electrode and an Ag/AgCl (3M KCl) was the reference electrode.

X-ray Crystallographic Study. Crystal data for compound **1** was collected on a SMART APEX II-CCD single crystal X-ray diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 273(2) K. The structure for compound **1** was solved by direct methods using the program SHELXS-97 and refined by full-matrix least-squares methods

on F^2 using the SHELXL-97 program package. All of the non-hydrogen atoms were refined anisotropically. Positions of the hydrogen atoms attached to carbon atoms were fixed at their ideal positions. During the refinement, the lighter atoms (O43, O44, C83, C88 and C89) were refined with the restrained command 'ISOR' so as to avoid their abnormal thermal parameters in three directions (U_{11}, U_{12} and U_{13}). Such refinement led to a least-squares restraint number of 30. A summary of the crystallographic data and structural determination for **1** is provided in Table S1. Selected bond lengths and angles for **1** is listed in Table S2.

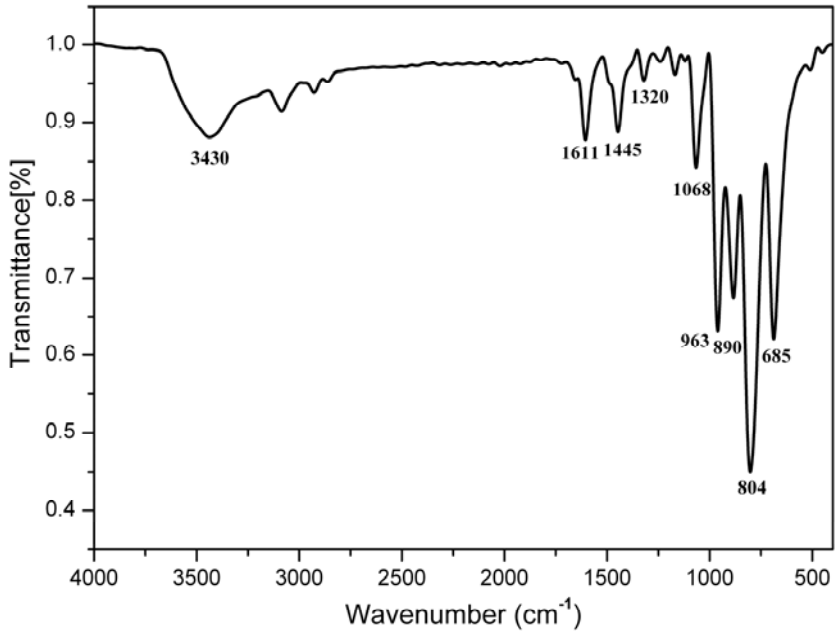

Fig. S1 The IR spectrum of **1**. In the IR spectrum of **1** (see Fig.S1, ESI†), strong peaks at 1068, 963, 890, and 797 cm^{-1} are due to ν_{as} (P-O), ν_{as}(Mo=O_d) , ν_{as}(Mo-O_b-Mo) and ν_{as}(Mo-O_c-Mo),[15] while bands at 1611, 1445, 1320, 1240, and 1167 cm^{-1} are ascribed to the bpy ligand.

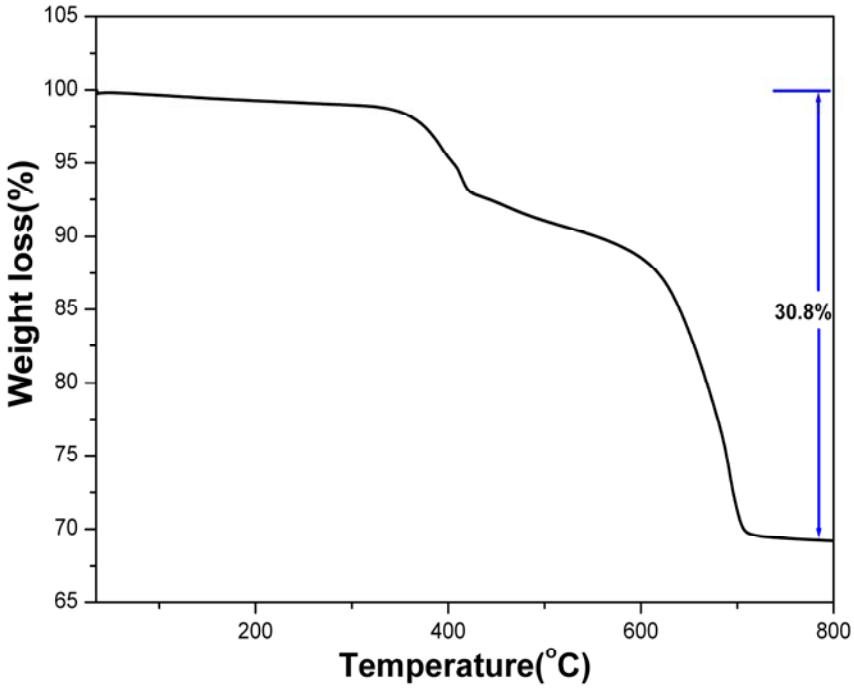

Fig. S2 The TG curve of **1**. The TG curve of **1** exhibits two weight-loss steps, attributing to the loss of bpy ligands and P_2O_5, respectively. The total weight loss is about 30.8%, in consistent with the calculated value of 31.5%. Its high thermal stability before 350 ^{o}C and extremely low solubility in various solvents as well as the POM-enriched character suggest that **1** could be an ideal hybrid material for electrocatalysis.

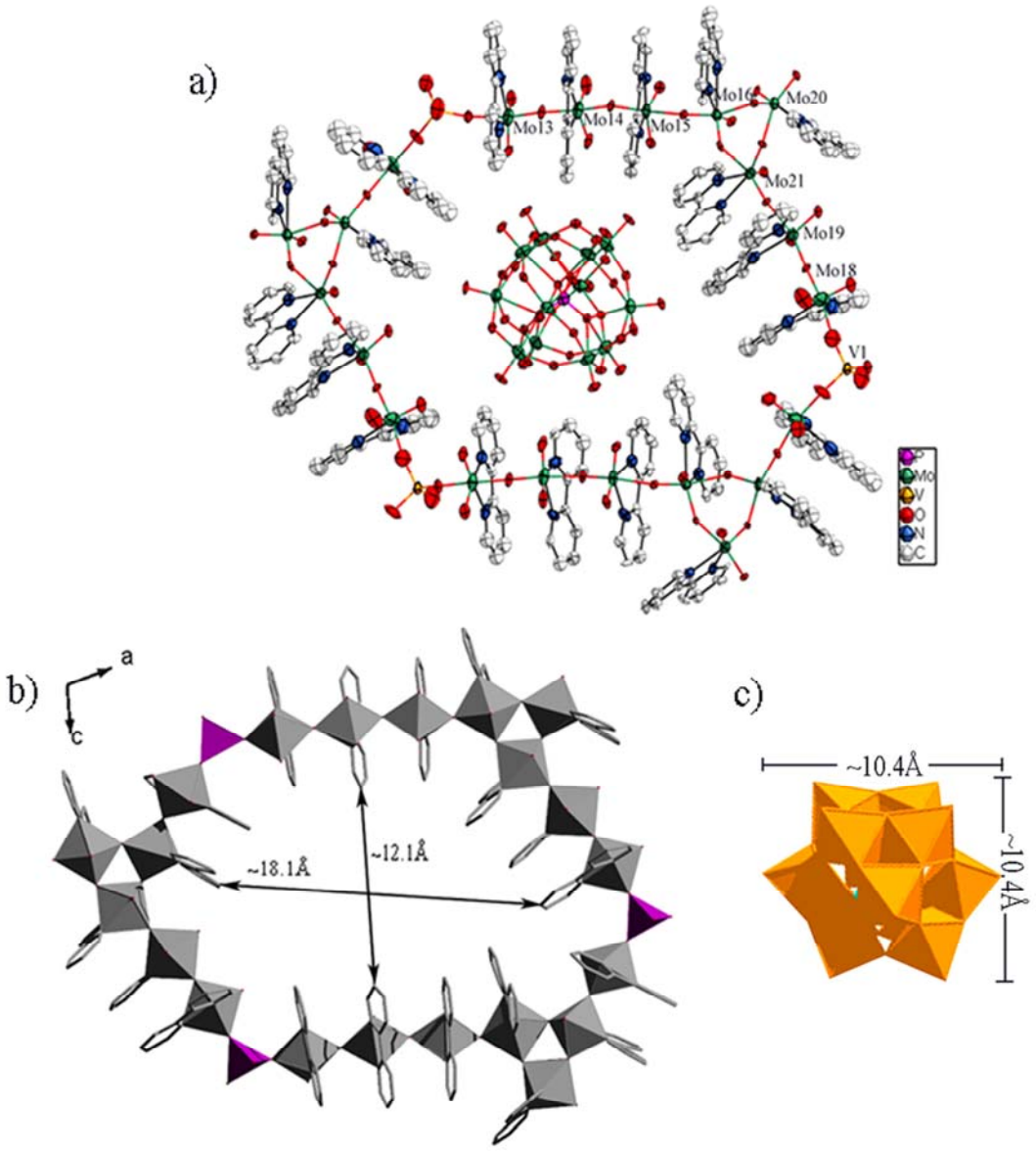

Fig. S3 (a) ORTEP plot of **1** with 50% thermal ellipsoids. The H atoms are omitted for clarity; (b)View of the pore size of 2-D network "host" in **1**; (c) View of the size of the Keggin-type polyoxoanion.

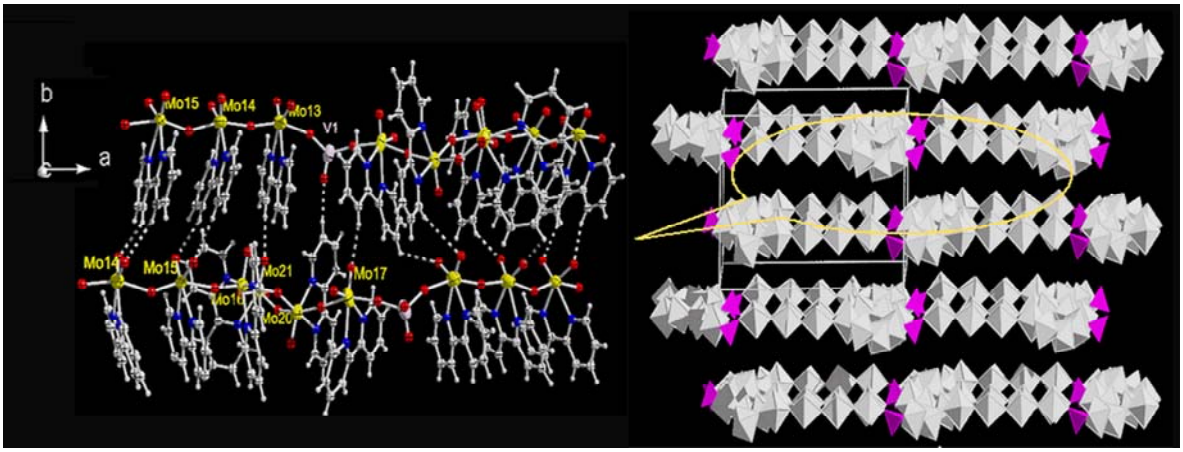

Fig. S4 View of the extensive H-bonds between C-H groups of bpy ligands and oxygen atoms of neighbouring hybrid metal oxide layer. A summary of C-H...O hydrogen bond lengths and angles is listed as follows.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(14)-H(14A)...O(11)	0.93 (1)	2.77 (8)	3.473 (2)	133 (9)
C(17)-H(17A)...O(16)	0.93 (1)	2.58 (9)	3.449(2)	155(9)
C(71)-H(71A)...O(25)	0.93 (1)	2.90(1)	3.495(2)	123 (9)
C(43)-H(43A)...O(24)	0.93(2)	2.83(1)	3.285(3)	111 (1)
C(79)-H(79A)...O(28)	0.93(2)	2.31(2)	3.199 (2)	161 (1)
C(7)-H(7A)...O(1)	0.93 (2)	2.39 (9)	3.294 (2)	163 (1)
C(4)-H(4A)...O(17)	0.93(2)	2.44(8)	2.973(2)	117(9)
C(27)-H(27A)...O(6)	0.93(1)	2.43(9)	3.251 (2)	148(9)
C(44)-H(44A)...O(4)	0.93(2)	2.47(1)	3.112(2)	127(1)
C(89)-H(89A)...O(3)	0.93(1)	2.64(9)	2.992(2)	103(9)

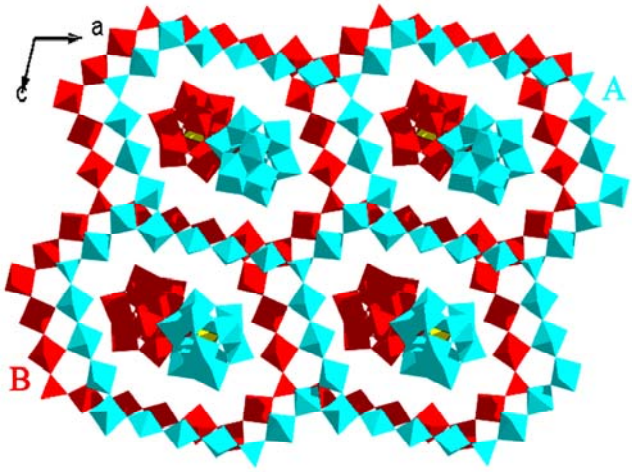

Fig. S5 View of the stacking mode between two adjacent layers of **1** along the *b* axis. Layer A (blue, upper), layer B (red, below).

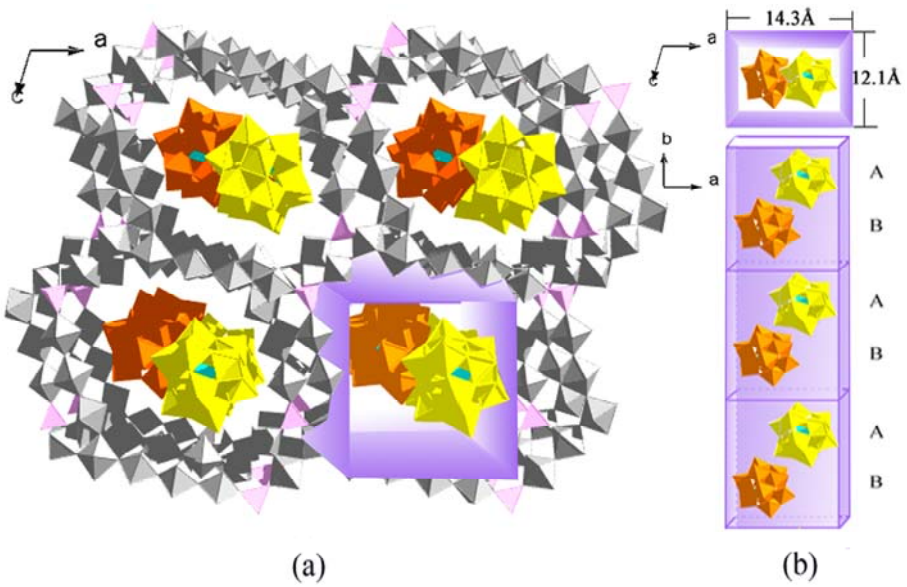

Fig. S6 (a) View of the 3-D composite Mo/V-oxide ‘‘host’’ encapsulating the Keggin ion “guests” in **1**. (b) View of the arrangement of Keggin ions in the tunnels. The polyanions in layer A, yellow; in layer B orange.

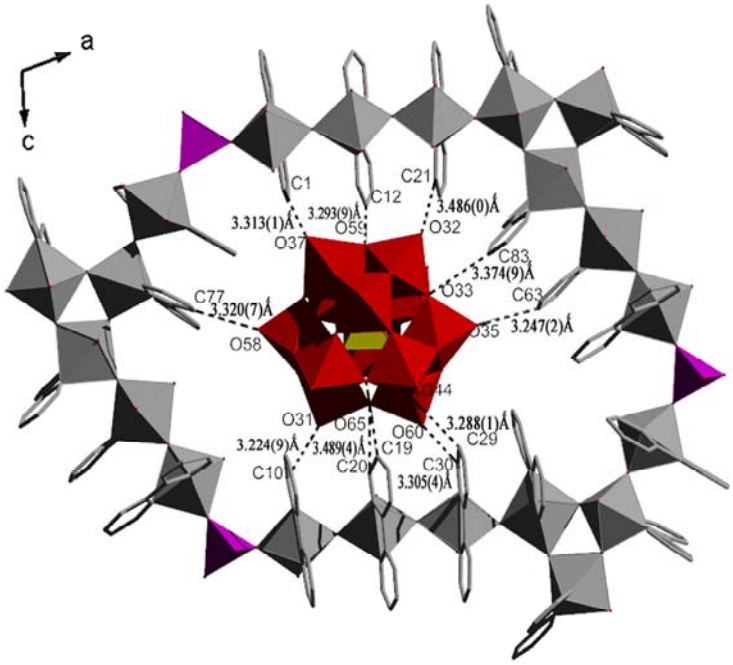

Fig. S7 View of the H-bonds between the surface oxygen atoms of Keggin-ions and inner organic ligand surface of the composite host. A summary of C-H...O hydrogen bond lengths and angles is listed as follows.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(63)-H(63A)...O(35)	0.93 (2)	2.74(9)	3.247 (2)	116(1)
C(83)-H(83A)...O(33)	0.93(2)	2.53(9)	3.375(2)	152(9)
C(21)-H(21A)...O(32)	0.93 (2)	2.63 (1)	3.486 (2)	153(9)
C(12)-H(12A)...O(59)	0.93(2)	2.75(9)	3.294(2)	119(1)
C(1)-H(1A)...O(37)	0.93(2)	2.46(8)	3.313 (2)	153(1)
C(77)-H(77A)...O(58)	0.93 (1)	2.40 (9)	3.321(2)	170(1)
C(10)-H(10A)...O(31)	0.93 (2)	2.70(1)	3.225(2)	117(9)
C(20)-H(20A)...O(65)	0.93(2)	2.81 (8)	3.489 (2)	131(9)
C(19)-H(19A)...O(54)	0.93(2)	2.55(7)	3.472 (2)	174(1)
C(30)-H(30A)...O(60)	0.93 (1)	2.47 (8)	3.305 (2)	149(9)
C(29)-H(29A)...O(44)	0.93(1)	2.66(7)	3.288 (1)	126(9)

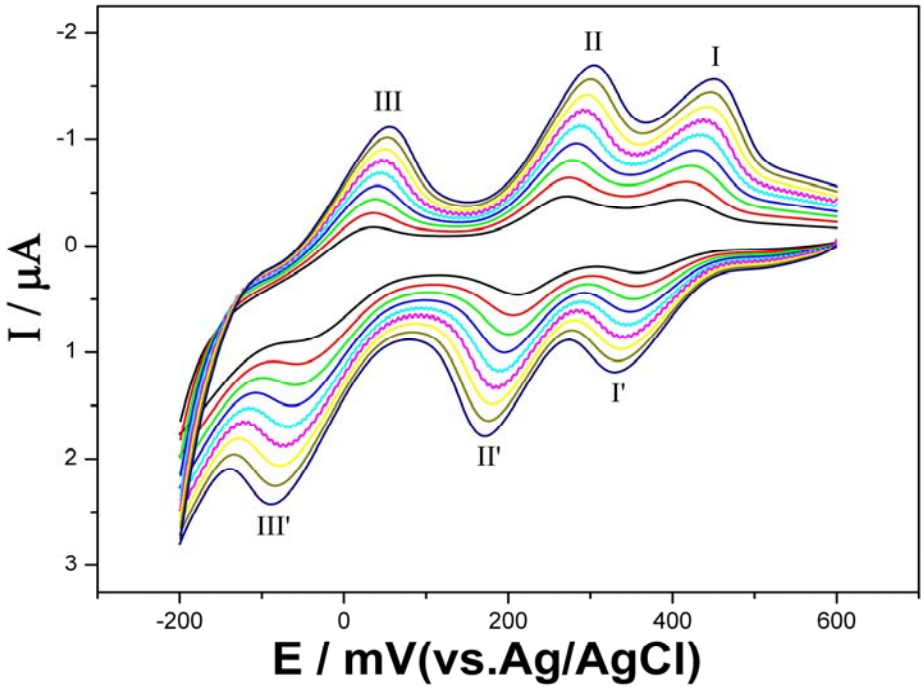

Fig. S8 Cyclic voltammograms of the **1-CPE** in the 1 M H_2SO_4 solution at different scan rates (from inner to outer: 100, 150, 200, 250, 300, 350, 400, 450, 500 mV s^{-1}). Potentials vs. Ag/AgCl; The CV of **1-CPE** shows three reversible redox peaks in the potential range +600 to -200 mV. The mean peak potentials E1/2=(Epa+Epc)/2 are +387.5, +240.0 and -11.0 mV, respectively (based on the CV at 200 mV s^{-1}). The redox peaks I–I', II–II' and III–III' correspond to reduction and re-oxidation of $[PMo_{12}O_{40}]^{3-}$ in **1** through two-, four- and six-electron process, respectively. The three redox peaks are consistent with those of reported $[PMo_{12}O_{40}]^{3-}$ polyoxoanions.

Table S1 Crystal data and structure refinement for **1**

Compounds	**1**
Empirical formula	$C_{90}H_{72}Mo_{21}N_{18}O_{68}PV$
Formula weight	4590.31
Temperature (K)	273(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
space group	$P2_1/c$
a	23.278(5)
b	15.790(4)
c	36.322(8)
α (°)	90
β	105.695(4)
γ (°)	90
V(Å^3)	12853(5)
Z	4
Calculated density (Mg/m3)	2.372
Absorption coefficient (mm-1)	2.155
F (000)	8808
Crystal size (mm)	0.29 x 0.27 x 0.25
Theta range for data collection (°)	1.76 ≤θ≤ 25.00
Limiting indices	-27≤ h≤ 24, -18≤ k≤ 18, -26≤ l≤ 43
Reflections collected / unique	63673 / 22623 [R(int) = 0.1356]
Max. and min. transmission	0.6148 and 0.5738
Goodness-of-fit on F2	0.945
Final R indices [I > 2 σ (I)][a]	R_1 = 0.0644, wR_2 = 0.1186
R indices (all data)[b]	R_1 = 0.1768, wR_2 = 0.1673
Largest diff. peak and hole (eÅ-3)	1.433 and -1.622

[a] $R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$; [b] $wR_2 = \Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0^2)^2]^{1/2}$

Table S2 Selected Bond lengths [Å] and angles [°] for **1**.

Mo(1)-O(17)	1.642(8)	Mo(2)-O(32)	1.650(9)
Mo(1)-O(28)	1.855(9)	Mo(2)-O(9)	1.884(9)
Mo(1)-O(38)	1.885(9)	Mo(2)-O(24)	1.894(10)
Mo(1)-O(35)	1.946(9)	Mo(2)-O(6)	1.909(10)
Mo(1)-O(39)	1.966(10)	Mo(2)-O(21)	1.961(9)
Mo(1)-O(27)	2.410(8)	Mo(2)-O(1)	2.433(8)
Mo(3)-O(30)	1.673(9)	Mo(4)-O(29)	1.662(8)
Mo(3)-O(24)	1.887(9)	Mo(4)-O(35)	1.903(9)
Mo(3)-O(11)	1.899(10)	Mo(4)-O(40)	1.906(10)
Mo(3)-O(40)	1.914(9)	Mo(4)-O(20)	1.908(9)
Mo(3)-O(23)	1.925(9)	Mo(4)-O(18)	1.915(9)
Mo(3)-O(25)	2.422(9)	Mo(4)-O(25)	2.417(9)
Mo(5)-O(36)	1.672(9)	Mo(6)-O(26)	1.677(9)
Mo(5)-O(21)	1.833(9)	Mo(6)-O(10)	1.884(9)
Mo(5)-O(11)	1.894(9)	Mo(6)-O(8)	1.886(8)
Mo(5)-O(34)	1.913(9)	Mo(6)-O(4)	1.911(8)
Mo(5)-O(14)	1.959(8)	Mo(6)-O(9)	1.932(9)
Mo(5)-O(31)	2.440(8)	Mo(6)-O(1)	2.467(9)
Mo(7)-O(15)	1.660(9)	Mo(8)-O(33)	1.661(8)
Mo(7)-O(4)	1.878(8)	Mo(8)-O(14)	1.879(8)
Mo(7)-O(13)	1.896(8)	Mo(8)-O(20)	1.880(9)
Mo(7)-O(23)	1.913(9)	Mo(8)-O(19)	1.934(9)
Mo(7)-O(18)	1.923(9)	Mo(8)-O(28)	1.975(9)
Mo(7)-O(25)	2.443(9)	Mo(8)-O(31)	2.456(9)
Mo(9)-O(3)	1.655(9)	Mo(10)-O(22)	1.656(9)
Mo(9)-O(39)	1.899(9)	Mo(10)-O(7)	1.874(8)
Mo(9)-O(12)	1.906(9)	Mo(10)-O(2)	1.887(9)
Mo(9)-O(13)	1.909(9)	Mo(10)-O(12)	1.909(9)
Mo(9)-O(8)	1.910(8)	Mo(10)-O(38)	1.941(9)
Mo(9)-O(27)	2.423(9)	Mo(10)-O(27)	2.436(9)
Mo(11)-O(37)	1.650(9)	Mo(12)-O(16)	1.656(9)
Mo(11)-O(5)	1.874(9)	Mo(12)-O(2)	1.887(9)
Mo(11)-O(6)	1.894(9)	Mo(12)-O(34)	1.912(9)
Mo(11)-O(7)	1.913(9)	Mo(12)-O(19)	1.930(8)
Mo(11)-O(10)	1.949(9)	Mo(12)-O(5)	1.930(9)
Mo(11)-O(1)	2.428(9)	Mo(12)-O(31)	2.410(9)
P(1)-O(1)	1.508(9)	P(1)-O(25)	1.535(9)
P(1)-O(31)	1.527(9)	P(1)-O(27)	1.544(9)
Mo(13)-O(47)	1.685(10)	Mo(14)-O(50)	1.695(10)
Mo(13)-O(46)	1.708(10)	Mo(14)-O(49)	1.693(11)
Mo(13)-O(45)	1.878(8)	Mo(14)-O(45)	1.900(8)
Mo(13)-O(41)	2.045(9)	Mo(14)-O(48)	1.984(8)

Mo(13)-N(2)	2.296(13)	Mo(14)-N(4)	2.316(12)
Mo(13)-N(1)	2.316(12)	Mo(14)-N(3)	2.343(12)
Mo(15)-O(51)	1.704(9)	Mo(16)-O(56)	1.693(9)
Mo(15)-O(52)	1.705(9)	Mo(16)-O(53)	1.741(8)
Mo(15)-O(48)	1.828(8)	Mo(16)-O(55)	1.788(8)
Mo(15)-O(53)	2.140(8)	Mo(16)-O(54)	2.173(8)
Mo(15)-N(5)	2.304(11)	Mo(16)-N(8)	2.297(10)
Mo(15)-N(6)	2.307(10)	Mo(16)-N(7)	2.313(11)
Mo(17)-O(59)	1.666(9)	Mo(18)-O(61)	1.681(9)
Mo(17)-O(54)	1.768(8)	Mo(18)-O(60)	1.768(8)
Mo(17)-O(57)	1.785(8)	Mo(18)-O(58)	1.795(8)
Mo(17)-O(58)	2.056(8)	Mo(18)-O(55)	2.107(8)
Mo(17)-N(9)	2.281(11)	Mo(18)-N(12)	2.261(11)
Mo(17)-N(10)	2.280(11)	Mo(18)-N(11)	2.287(11)
Mo(19)-O(63)	1.695(10)	Mo(20)-O(66)	1.681(14)
Mo(19)-O(64)	1.712(9)	Mo(20)-O(65)	1.694(10)
Mo(19)-O(62)	1.840(9)	Mo(20)-O(62)	1.899(9)
Mo(19)-O(60)	2.064(8)	Mo(20)-O(43)#1	1.955(16)
Mo(19)-N(14)	2.319(12)	Mo(20)-N(15)	2.330(14)
Mo(19)-N(13)	2.324(12)	Mo(20)-N(16)	2.349(13)
Mo(21)-O(67)	1.703(13)	Mo(21)-O(57)	1.992(9)
Mo(21)-O(68)	1.721(13)	Mo(21)-N(17)	2.295(19)
Mo(21)-O(42)#2	1.863(13)	Mo(21)-N(18)	2.32(2)
O(42)-Mo(21)#3	1.863(13)	O(43)-Mo(20)#4	1.955(16)
V(1)-O(44)	1.414(19)	V(1)-O(41)	1.674(9)
V(1)-O(43)	1.637(16)	V(1)-O(42)	1.703(14)
O(47)-Mo(13)-O(46)	107.4(6)	O(50)-Mo(14)-O(49)	107.0(6)
O(47)-Mo(13)-O(45)	100.3(4)	O(50)-Mo(14)-O(45)	101.0(4)
O(46)-Mo(13)-O(45)	102.8(5)	O(49)-Mo(14)-O(45)	99.2(5)
O(47)-Mo(13)-O(41)	94.2(4)	O(50)-Mo(14)-O(48)	91.8(4)
O(46)-Mo(13)-O(41)	90.6(4)	O(49)-Mo(14)-O(48)	92.3(4)
O(45)-Mo(13)-O(41)	156.3(4)	O(45)-Mo(14)-O(48)	159.3(4)
O(47)-Mo(13)-N(2)	161.6(5)	O(50)-Mo(14)-N(4)	155.7(5)
O(46)-Mo(13)-N(2)	90.1(5)	O(49)-Mo(14)-N(4)	94.0(6)
O(45)-Mo(13)-N(2)	80.8(4)	O(45)-Mo(14)-N(4)	87.1(4)
O(41)-Mo(13)-N(2)	79.6(4)	O(48)-Mo(14)-N(4)	74.9(4)
O(47)-Mo(13)-N(1)	92.8(5)	O(50)-Mo(14)-N(3)	89.3(5)
O(46)-Mo(13)-N(1)	158.0(5)	O(49)-Mo(14)-N(3)	161.3(5)
O(45)-Mo(13)-N(1)	81.5(4)	O(45)-Mo(14)-N(3)	86.1(4)
O(41)-Mo(13)-N(1)	79.0(4)	O(48)-Mo(14)-N(3)	77.8(4)
N(2)-Mo(13)-N(1)	69.1(5)	N(4)-Mo(14)-N(3)	68.2(4)
O(51)-Mo(15)-O(52)	106.3(5)	O(56)-Mo(16)-O(53)	104.0(4)

O(51)-Mo(15)-O(48)	103.8(4)	O(56)-Mo(16)-O(55)	106.4(4)
O(52)-Mo(15)-O(48)	105.5(4)	O(53)-Mo(16)-O(55)	103.3(4)
O(51)-Mo(15)-O(53)	90.0(4)	O(56)-Mo(16)-O(54)	89.9(4)
O(52)-Mo(15)-O(53)	88.5(4)	O(53)-Mo(16)-O(54)	160.0(4)
O(48)-Mo(15)-O(53)	156.2(4)	O(55)-Mo(16)-O(54)	86.0(3)
O(51)-Mo(15)-N(5)	90.4(5)	O(56)-Mo(16)-N(8)	154.1(4)
O(52)-Mo(15)-N(5)	156.0(4)	O(53)-Mo(16)-N(8)	87.3(4)
O(48)-Mo(15)-N(5)	86.4(4)	O(55)-Mo(16)-N(8)	93.1(4)
O(53)-Mo(15)-N(5)	74.1(3)	O(54)-Mo(16)-N(8)	74.4(3)
O(51)-Mo(15)-N(6)	157.9(4)	O(56)-Mo(16)-N(7)	87.7(4)
O(52)-Mo(15)-N(6)	90.7(4)	O(53)-Mo(16)-N(7)	86.5(4)
O(48)-Mo(15)-N(6)	84.5(4)	O(55)-Mo(16)-N(7)	159.9(4)
O(53)-Mo(15)-N(6)	76.1(3)	O(54)-Mo(16)-N(7)	79.8(3)
N(5)-Mo(15)-N(6)	69.4(4)	N(8)-Mo(16)-N(7)	69.5(4)
O(59)-Mo(17)-O(54)	107.2(4)	O(61)-Mo(18)-O(60)	103.5(4)
O(59)-Mo(17)-O(57)	102.9(5)	O(61)-Mo(18)-O(58)	106.4(4)
O(54)-Mo(17)-O(57)	101.5(4)	O(60)-Mo(18)-O(58)	101.7(4)
O(59)-Mo(17)-O(58)	94.9(4)	O(61)-Mo(18)-O(55)	90.3(4)
O(54)-Mo(17)-O(58)	86.5(3)	O(60)-Mo(18)-O(55)	161.7(4)
O(57)-Mo(17)-O(58)	157.2(4)	O(58)-Mo(18)-O(55)	85.5(3)
O(59)-Mo(17)-N(9)	84.3(4)	O(61)-Mo(18)-N(12)	88.8(4)
O(54)-Mo(17)-N(9)	158.3(4)	O(60)-Mo(18)-N(12)	88.3(4)
O(57)-Mo(17)-N(9)	93.5(4)	O(58)-Mo(18)-N(12)	158.9(4)
O(58)-Mo(17)-N(9)	74.0(3)	O(55)-Mo(18)-N(12)	79.9(3)
O(59)-Mo(17)-N(10)	154.5(4)	O(61)-Mo(18)-N(11)	158.3(4)
O(54)-Mo(17)-N(10)	96.7(4)	O(60)-Mo(18)-N(11)	85.8(4)
O(57)-Mo(17)-N(10)	80.4(4)	O(58)-Mo(18)-N(11)	90.5(4)
O(58)-Mo(17)-N(10)	77.4(4)	O(55)-Mo(18)-N(11)	77.2(3)
N(9)-Mo(17)-N(10)	70.2(4)	N(12)-Mo(18)-N(11)	71.6(4)
O(63)-Mo(19)-O(64)	107.1(4)	O(66)-Mo(20)-O(65)	108.0(7)
O(63)-Mo(19)-O(62)	101.4(5)	O(66)-Mo(20)-O(62)	97.4(6)
O(64)-Mo(19)-O(62)	102.7(4)	O(65)-Mo(20)-O(62)	97.0(5)
O(63)-Mo(19)-O(60)	92.2(4)	O(66)-Mo(20)-O(43)#1	97.6(8)
O(64)-Mo(19)-O(60)	91.2(4)	O(65)-Mo(20)-O(43)#1	97.7(6)
O(62)-Mo(19)-O(60)	156.6(4)	O(62)-Mo(20)-O(43)#1	154.6(5)
O(63)-Mo(19)-N(14)	158.4(4)	O(66)-Mo(20)-N(15)	159.2(6)
O(64)-Mo(19)-N(14)	91.5(4)	O(65)-Mo(20)-N(15)	92.6(6)
O(62)-Mo(19)-N(14)	84.8(4)	O(62)-Mo(20)-N(15)	76.6(4)
O(60)-Mo(19)-N(14)	76.1(4)	O(43)#1-Mo(20)-N(15)	82.2(6)
O(63)-Mo(19)-N(13)	91.1(4)	O(66)-Mo(20)-N(16)	91.6(6)
O(64)-Mo(19)-N(13)	159.4(5)	O(65)-Mo(20)-N(16)	160.3(6)
O(62)-Mo(19)-N(13)	82.5(4)	O(62)-Mo(20)-N(16)	80.5(4)
O(60)-Mo(19)-N(13)	78.3(4)	O(43)#1-Mo(20)-N(16)	78.6(5)

N(14)-Mo(19)-N(13)	68.9(4)	N(15)-Mo(20)-N(16)	67.9(5)
O(67)-Mo(21)-O(68)	107.4(7)	O(68)-Mo(21)-N(17)	93.1(7)
O(67)-Mo(21)-O(42)#2	100.5(7)	O(42)#2-Mo(21)-N(17)	86.3(7)
O(68)-Mo(21)-O(42)#2	100.9(7)	O(57)-Mo(21)-N(17)	74.2(5)
O(67)-Mo(21)-O(57)	93.4(5)	O(67)-Mo(21)-N(18)	89.9(7)
O(68)-Mo(21)-O(57)	92.0(5)	O(68)-Mo(21)-N(18)	161.0(7)
O(42)#2-Mo(21)-O(57)	157.2(7)	O(42)#2-Mo(21)-N(18)	83.0(6)
O(67)-Mo(21)-N(17)	156.6(7)	O(57)-Mo(21)-N(18)	79.0(5)
N(17)-Mo(21)-N(18)	68.5(7)	O(44)-V(1)-O(43)	114.2(10)
O(44)-V(1)-O(42)	108.2(10)	O(44)-V(1)-O(41)	108.4(7)
O(43)-V(1)-O(42)	104.3(8)	O(43)-V(1)-O(41)	109.5(6)
O(41)-V(1)-O(42)	112.3(7)		

Symmetry transformations used to generate equivalent atoms: #1 x-1,-y+1/2,z-1/2 #2 x-1,y,z #3 x+1,y,z #4 x+1,-y+1/2,z+1/2