Supporting information

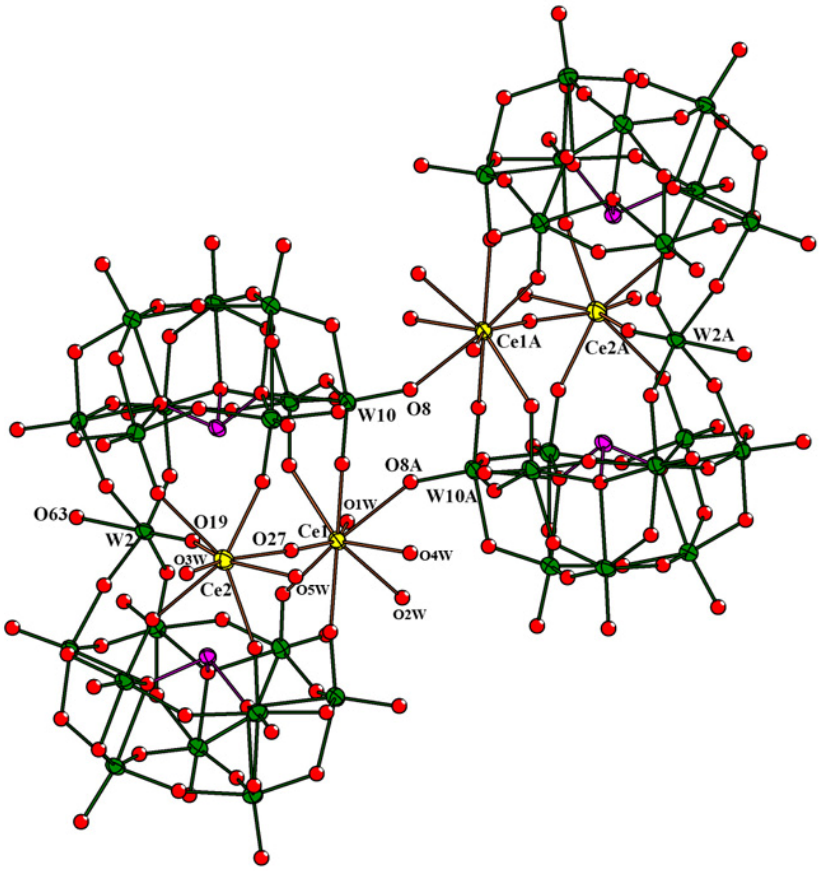


Fig. S1 ORTEP plot of the polyanion of **1** with 50% thermal ellipsoids for As, Ce and W. The atom labels "A" means -x,-y+2,-z.

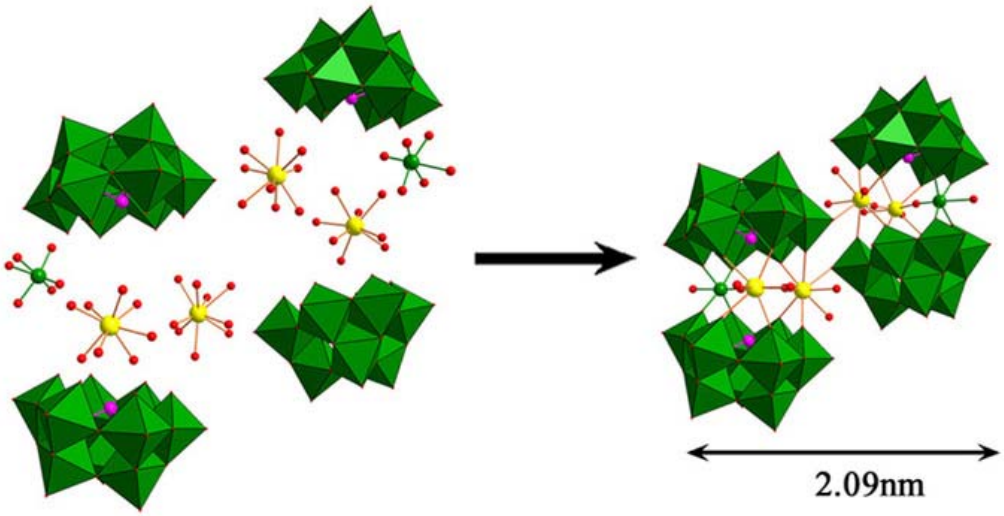


Fig. S2. Schematic view of the basic building blocks and their connection modes in the polyanion of **1**. W (green octahedra), Ce (yellow ball), As (purple ball), O (red ball).

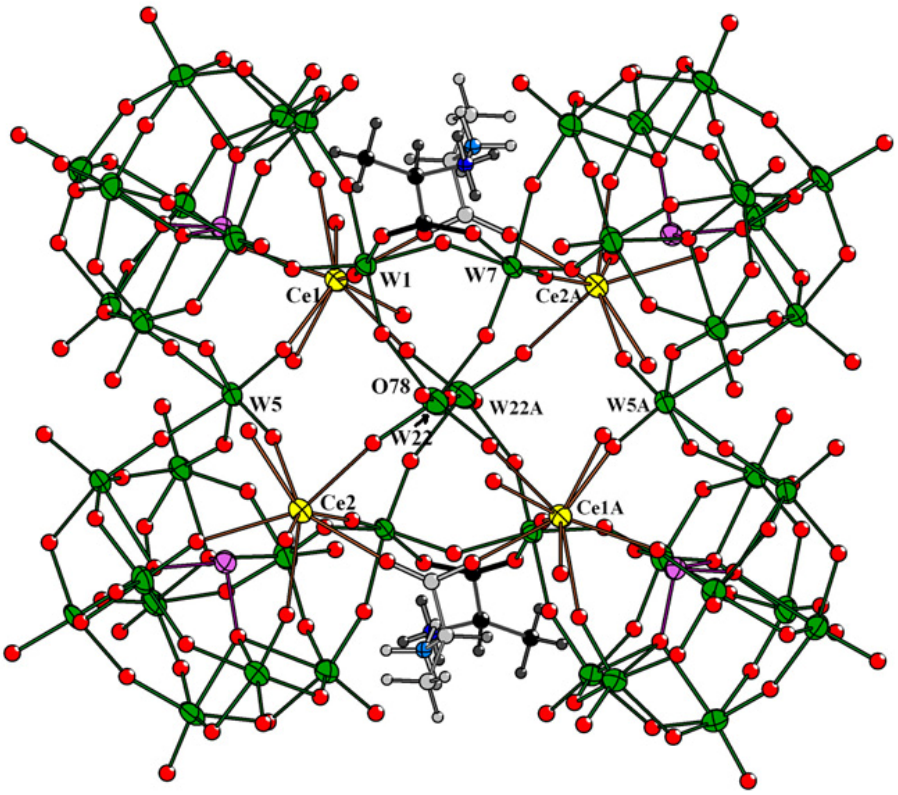


Fig. S3. ORTEP plot of the polyanion of **2** with 50% thermal ellipsoids for As, Ce and W. The atom labels "A" means -x+1,-y+1,-z+1.

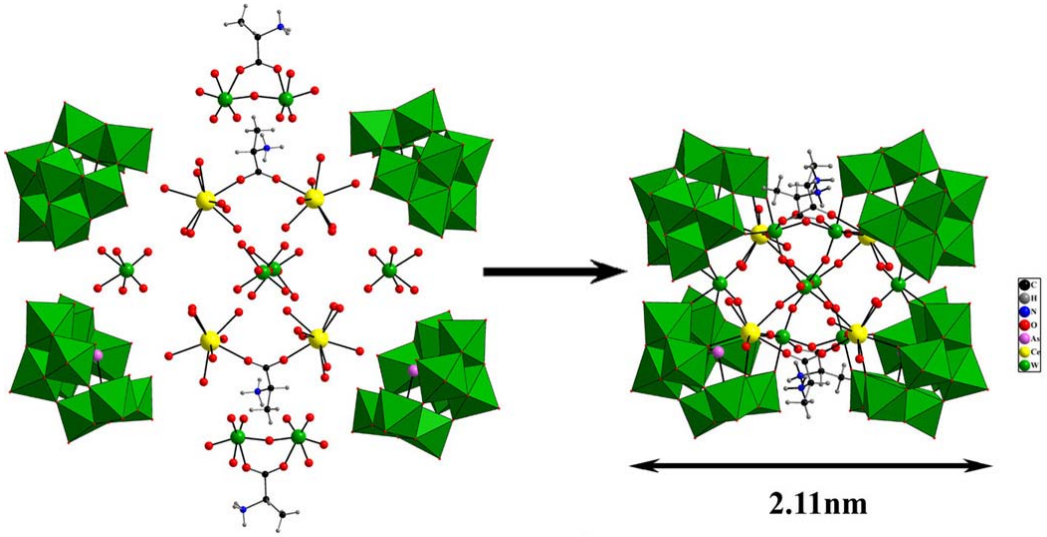


Fig. S4. Schematic view of the basic building blocks and their connection modes in the polyanion of **1**. W (green octahedra), Ce (yellow ball), As (purple ball), O (red ball).

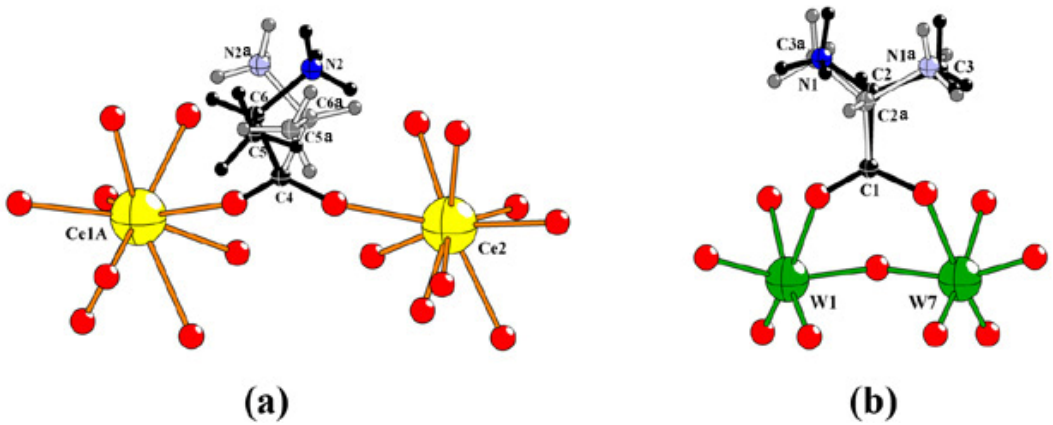


Fig. S5. Ball-and-stick view of the disordered alanines in the polyanion of **2.** W(green crossed ball), Ce (yellow crossed ball), O (red ball), C (blackcrossed ball), N (blue crossed ball), H (grey crossed ball). The atom labels "A" means -x+1,-y+1,-z+1.

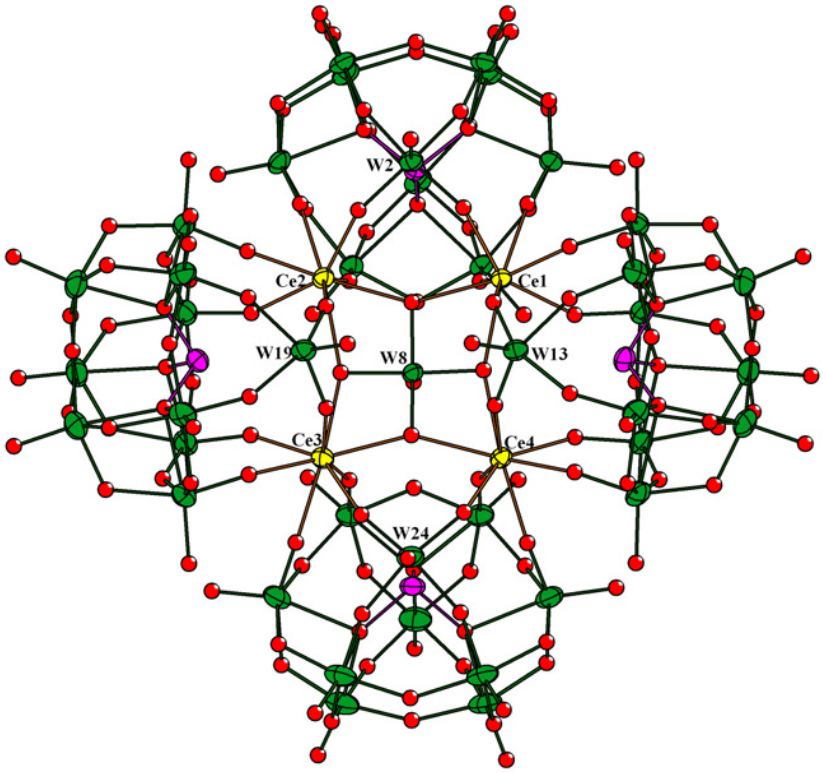


Fig. S6. ORTEP plot of the polyanion of **3** with 50% thermal ellipsoids for As, Ce and W.

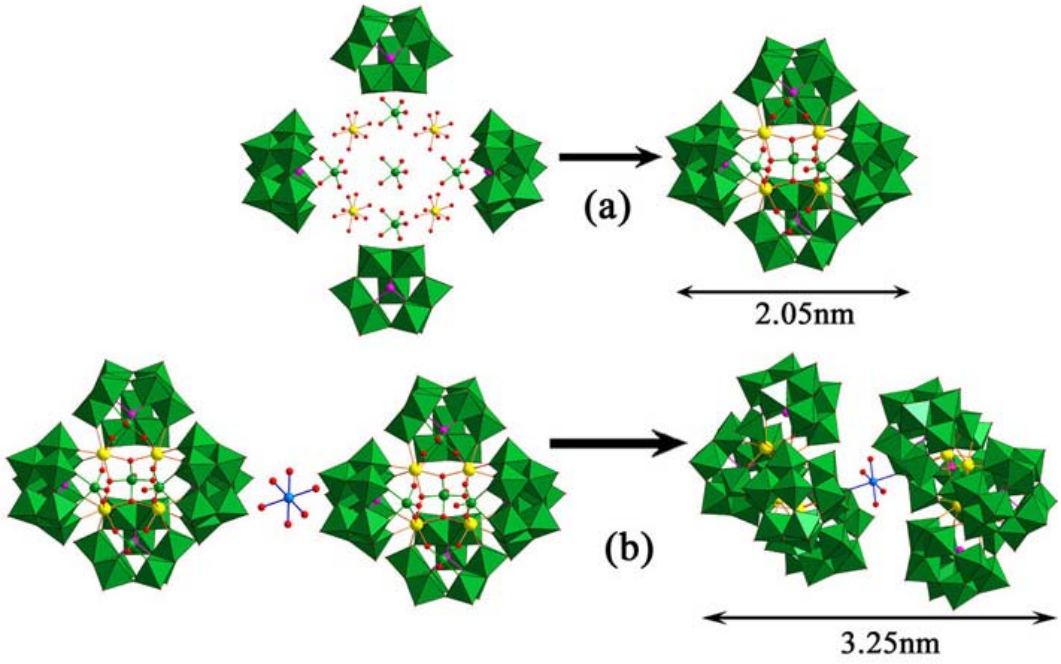
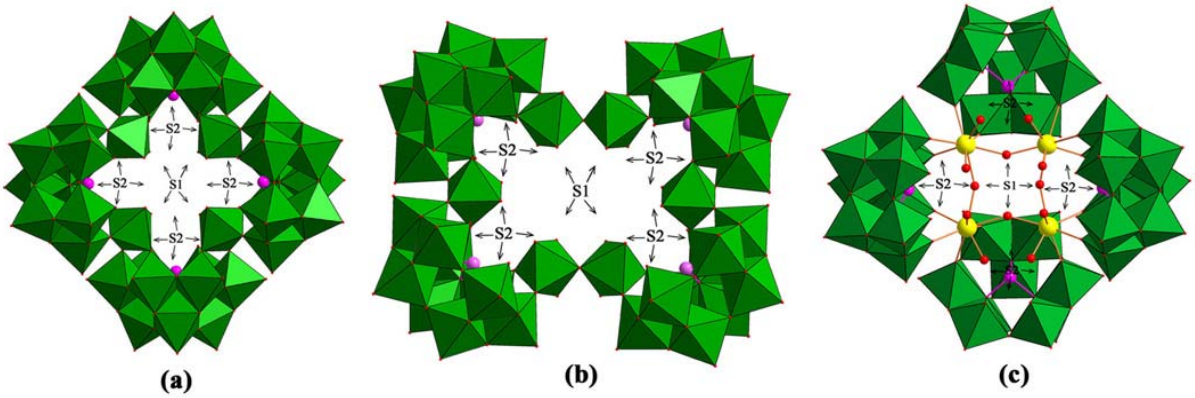


Fig. S7. Schematic view of the basic building blocks and their connection modes in the polyanion of **1**. W (green octahedra and ball), Ce (yellow ball), As (purple ball), O (red ball), Mn (blue ball).



Scheme S1 Schematic view of three kinds of cryptand-type clusters $[As_4W_{40}O_{140}]^{28-}$ (a), the circle part of the polyanion in **2** (b) and the circle part of the polyanions in **3 (c)**. S1 position means the central cryptate site and S2 position means the remnant vacant site at $\{AsW_9\}$ units.[2]

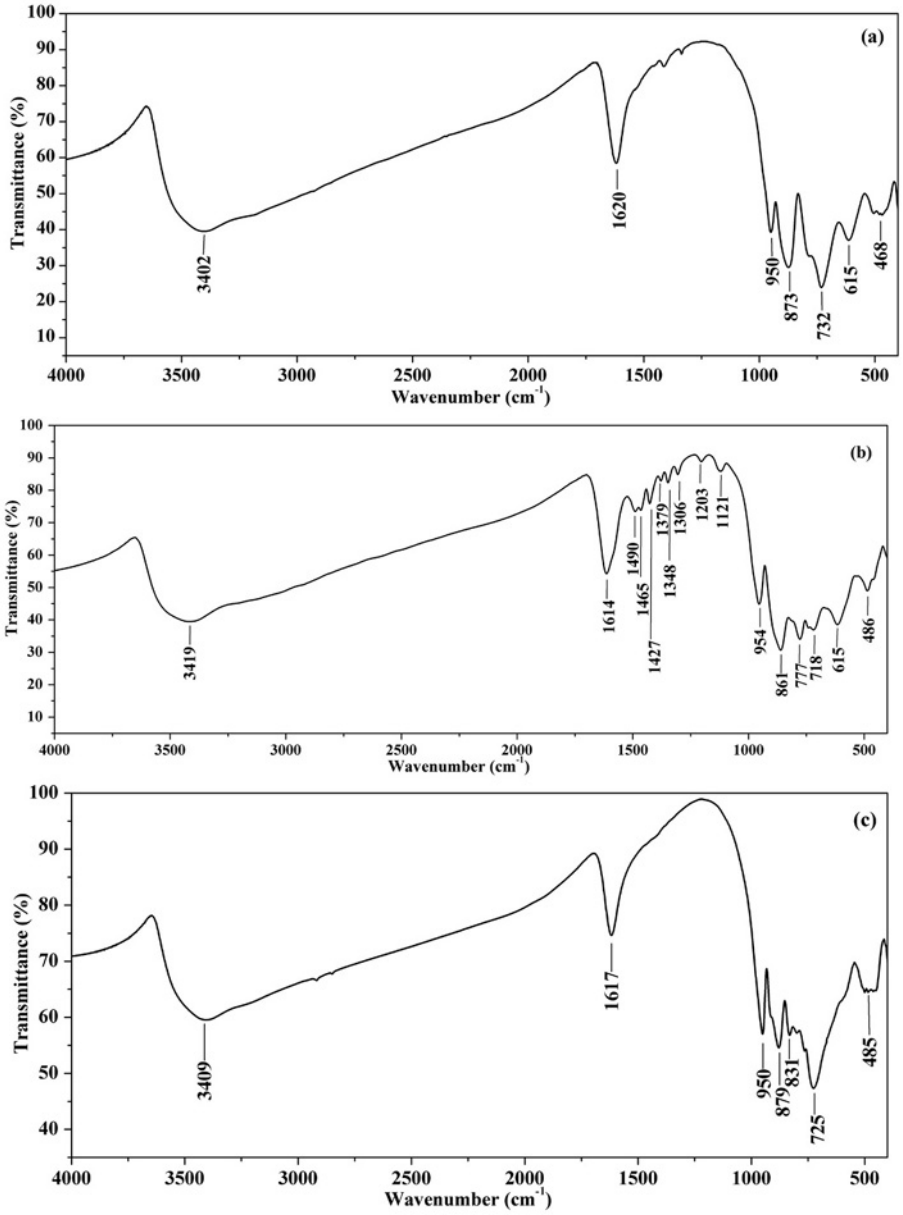


Fig. S8. IR spectrum of **1(a), 2(b) and 3(c).**

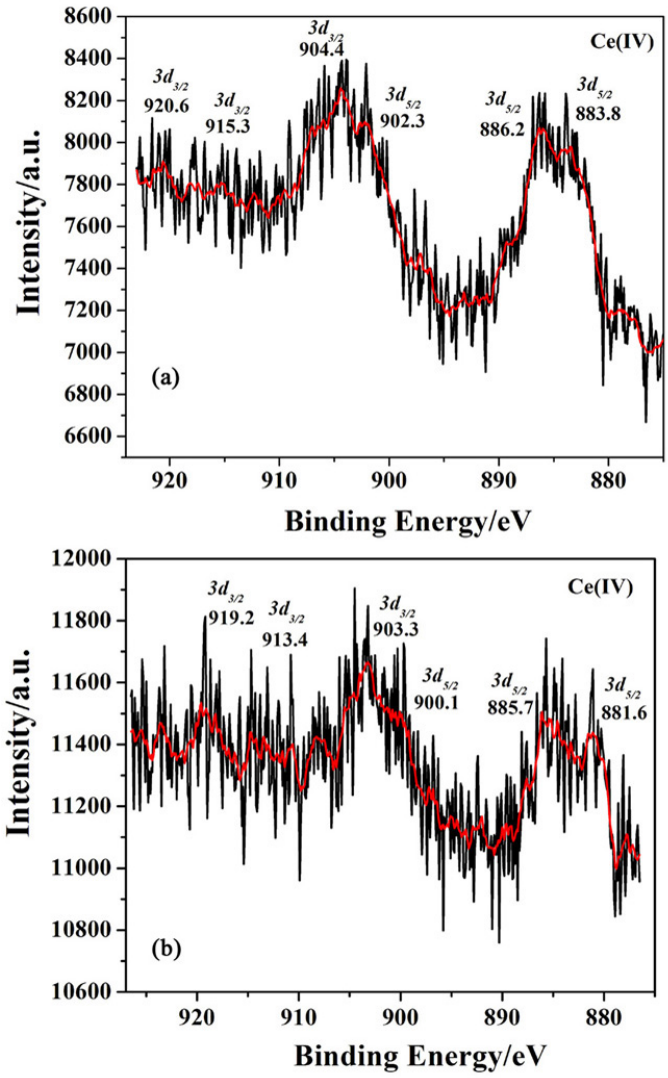


Fig. S9. The XPS spectrum of Ce3d for **2** (**a**) and **3** (**b**).

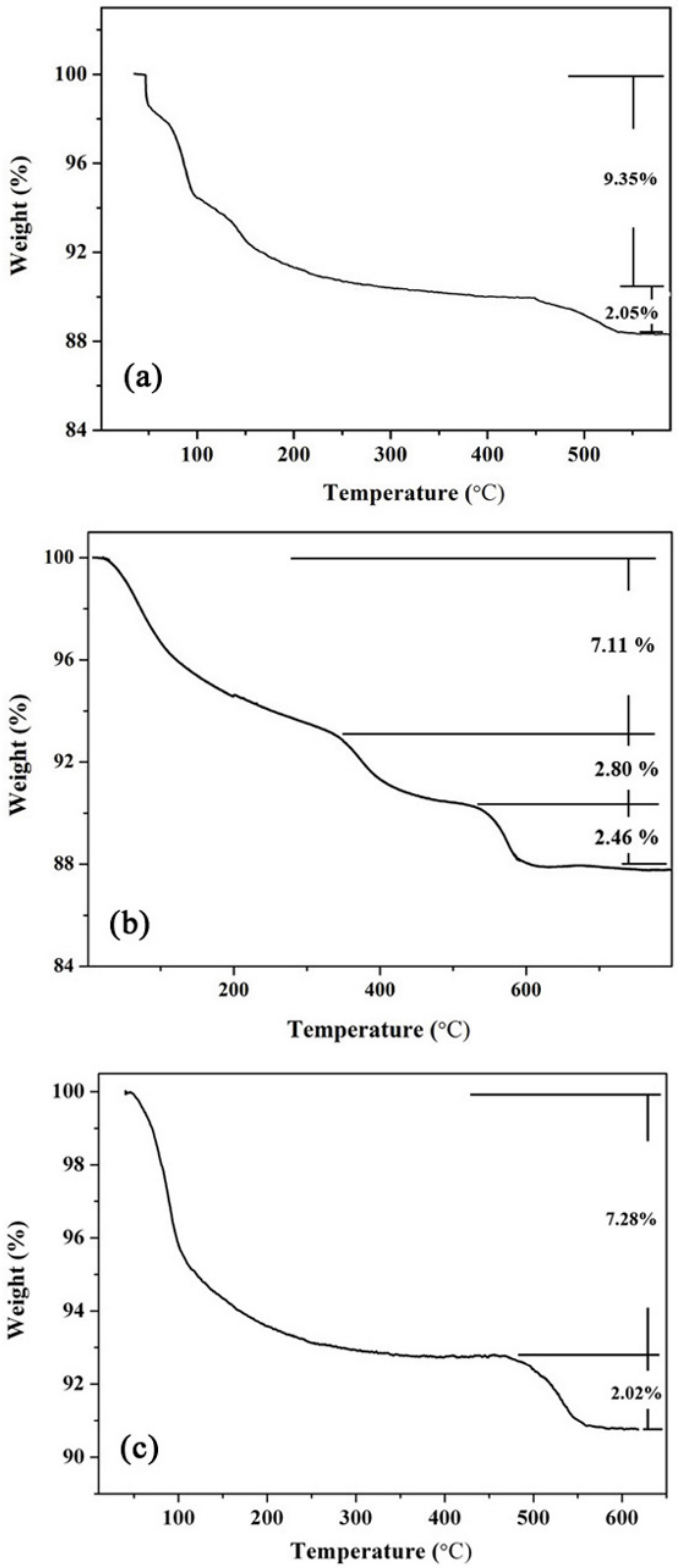


Fig. S10. The TG curve of **1 (a), 2(b) and 3(c)**

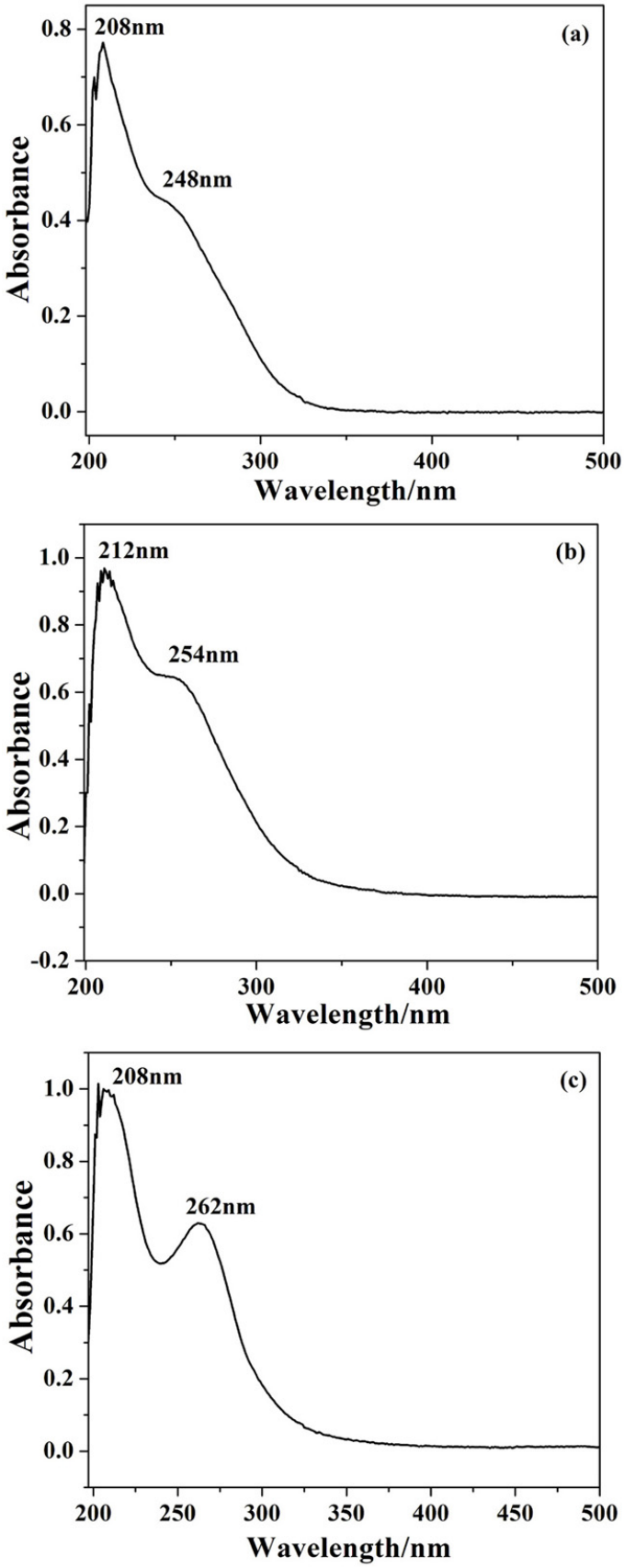


Fig. S11. The UV-vis spectrum of the sample in the H_2SO_4/Na_2SO_4 solution for **1** at pH = 3.0 (**a**), **2** at pH = 2.0 (**b**) and **3** at pH = 5.0 (**c**).

Table S1. Selected bond lengths (Å) and bond angles(º) of **1**

W(1)-O(2)	1.73(3)	W(2)-O(19)	1.72(2)	W(3)-O(45)	1.73(2)
W(1)-O(24)	1.78(2)	W(2)-O(29)	1.87(2)	W(3)-O(43)	1.86(2)
W(1)-O(23)	1.92(2)	W(2)-O(17)	1.88(2)	W(3)-O(21)	1.88(2)
W(1)-O(48)	2.00(2)	W(2)-O(9)	1.910(17)	W(3)-O(57)	1.92(2)
W(1)-O(31)	2.06(2)	W(2)-O(62)	1.94(2)	W(3)-O(29)	1.97(2)
W(1)-O(28)	2.30(2)	W(2)-O(63)	2.27(2)	W(3)-O(6)	2.383(19)
W(4)-O(46)	1.73(2)	W(5)-O(41)	1.68(2)	W(6)-O(67)	1.74(2)
W(4)-O(53)	1.81(2)	W(5)-O(52)	1.87(2)	W(6)-O(59)	1.85(2)
W(4)-O(40)	1.89(2)	W(5)-O(33)	1.90(2)	W(6)-O(60)	1.86(2)
W(4)-O(15)	1.944(19)	W(5)-O(15)	1.93(2)	W(6)-O(22)	1.93(2)
W(4)-O(60)	2.09(2)	W(5)-O(17)	1.95(2)	W(6)-O(52)	2.01(2)
W(4)-O(64)	2.30(2)	W(5)-O(64)	2.37(2)	W(6)-O(64)	2.37(2)
W(7)-O(50)	1.70(2)	W(8)-O(5)	1.73(2)	W(9)-O(61)	1.74(2)
W(7)-O(48)	1.86(2)	W(8)-O(68)	1.91(2)	W(9)-O(55)	1.858(19)
W(7)-O(30)	1.89(2)	W(8)-O(13)	1.92(2)	W(9)-O(31)	1.90(2)
W(7)-O(62)	1.92(2)	W(8)-O(9)	1.919(19)	W(9)-O(22)	1.94(2)
W(7)-O(33)	1.95(2)	W(8)-O(21)	1.94(2)	W(9)-O(30)	1.99(2)
W(7)-O(28)	2.34(2)	W(8)-O(65)	2.44(2)	W(9)-O(28)	2.32(2)
W(10)-O(8)	1.708(18)	W(11)-O(66)	1.76(2)	W(12)-O(4)	1.72(2)
W(10)-O(34)	1.72(2)	W(11)-O(49)	1.78(2)	W(12)-O(10)	1.865(17)
W(10)-O(36)	1.92(2)	W(11)-O(58)	1.89(2)	W(12)-O(14)	1.87(2)
W(10)-O(18)	1.95(2)	W(11)-O(68)	2.011(19)	W(12)-O(38)	1.95(2)
W(10)-O(69)	2.14(2)	W(11)-O(20)	2.05(2)	W(12)-O(43)	1.99(2)
W(10)-O(26)	2.341(19)	W(11)-O(65)	2.23(2)	W(12)-O(6)	2.324(18)
W(13)-O(54)	1.72(2)	W(14)-O(1)	1.75(2)	W(15)-O(11)	1.72(2)
W(13)-O(39)	1.79(2)	W(14)-O(47)	1.80(2)	W(15)-O(16)	1.74(2)
W(13)-O(18)	1.937(18)	W(14)-O(36)	1.915(19)	W(15)-O(40)	1.93(2)
W(13)-O(58)	1.95(2)	W(14)-O(57)	1.94(2)	W(15)-O(51)	1.96(2)
W(13)-O(25)	2.05(2)	W(14)-O(10)	2.025(19)	W(15)-O(56)	2.09(2)
W(13)-O(26)	2.33(2)	W(14)-O(6)	2.286(18)	W(15)-O(7)	2.34(2)
W(16)-O(44)	1.69(2)	W(17)-O(35)	1.70(2)	W(18)-O(42)	1.73(2)
W(16)-O(20)	1.83(2)	W(17)-O(32)	1.819(19)	W(18)-O(37)	1.743(19)
W(16)-O(12)	1.893(18)	W(17)-O(56)	1.87(2)	W(18)-O(23)	1.93(2)
W(16)-O(38)	1.91(2)	W(17)-O(55)	1.96(2)	W(18)-O(51)	1.96(2)
W(16)-O(13)	1.96(2)	W(17)-O(59)	1.97(2)	W(18)-O(32)	2.11(2)
W(16)-O(65)	2.386(19)	W(17)-O(7)	2.36(2)	W(18)-O(7)	2.367(18)
W(19)-O(3)	1.71(3)	Ce(1)-O(27)	2.310(19)	Ce(2)-O(27)	2.277(19)
W(19)-O(69)	1.79(2)	Ce(1)-O(24)	2.48(2)	Ce(2)-O(39)	2.43(2)
W(19)-O(25)	1.83(2)	Ce(1)-O(47)	2.48(2)	Ce(2)-O(3W)	2.47(3)
W(19)-O(12)	1.928(19)	Ce(1)-O(4W)	2.56(2)	Ce(2)-O(11)	2.48(2)
W(19)-O(14)	1.94(2)	Ce(1)-O(37)	2.58(2)	Ce(2)-O(53)	2.48(2)
W(19)-O(26)	2.42(2)	Ce(1)-O(34)	2.59(2)	Ce(2)-O(49)	2.52(2)

As(1)-O(26)	1.78(2)	Ce(1)-O(8A)	2.59(2)	Ce(2)-O(19)	2.60(2)
As(1)-O(65)	1.791(19)	Ce(1)-O(2W)	2.61(2)	Ce(2)-O(5W)	2.68(3)
As(1)-O(6)	1.80(2)	Ce(1)-O(1W)	2.81(3)		
As(2)-O(64)	1.80(2)	As(2)-O(7)	1.797(19)	As(2)-O(28)	1.81(2)
O(2)-W(1)-O(24)	102.3(12)	O(19)-W(2)-O(29)	100.3(10)	O(45)-W(3)-O(43)	100.9(10)
O(2)-W(1)-O(23)	102.0(11)	O(19)-W(2)-O(17)	96.9(10)	O(45)-W(3)-O(21)	100.0(10)
O(2)-W(1)-O(48)	97.8(11)	O(19)-W(2)-O(9)	96.4(9)	O(45)-W(3)-O(57)	101.7(10)
O(2)-W(1)-O(31)	97.7(11)	O(19)-W(2)-O(62)	100.6(9)	O(45)-W(3)-O(29)	101.7(10)
O(2)-W(1)-O(28)	165.1(10)	O(19)-W(2)-O(63)	175.0(9)	O(45)-W(3)-O(6)	171.8(10)
O(46)-W(4)-O(53)	103.1(11)	O(41)-W(5)-O(52)	100.5(10)	O(67)-W(6)-O(59)	101.5(10)
O(46)-W(4)-O(40)	102.8(10)	O(41)-W(5)-O(33)	99.9(10)	O(67)-W(6)-O(60)	100.8(10)
O(46)-W(4)-O(15)	97.0(9)	O(41)-W(5)-O(15)	102.5(10)	O(67)-W(6)-O(22)	102.2(10)
O(46)-W(4)-O(60)	96.4(10)	O(41)-W(5)-O(17)	100.1(10)	O(67)-W(6)-O(52)	97.2(9)
O(46)-W(4)-O(64)	165.8(9)	O(41)-W(5)-O(64)	173.7(10)	O(67)-W(6)-O(64)	169.7(8)
O(50)-W(7)-O(48)	101.1(11)	O(5)-W(8)-O(68)	101.1(10)	O(61)-W(9)-O(55)	103.0(9)
O(50)-W(7)-O(30)	98.7(10)	O(5)-W(8)-O(13)	99.1(10)	O(61)-W(9)-O(31)	99.7(9)
O(50)-W(7)-O(62)	103.1(10)	O(5)-W(8)-O(9)	101.4(9)	O(61)-W(9)-O(22)	103.2(9)
O(50)-W(7)-O(33)	99.3(10)	O(5)-W(8)-O(21)	102.5(10)	O(61)-W(9)-O(30)	96.5(9)
O(50)-W(7)-O(28)	170.7(9)	O(5)-W(8)-O(65)	171.8(9)	O(61)-W(9)-O(28)	167.5(9)
O(8)-W(10)-O(34)	104.1(10)	O(66)-W(11)-O(49)	103.9(11)	O(4)-W(12)-O(10)	100.6(10)
O(8)-W(10)-O(36)	100.0(9)	O(66)-W(11)-O(58)	103.4(11)	O(4)-W(12)-O(14)	101.4(10)
O(8)-W(10)-O(18)	101.6(9)	O(66)-W(11)-O(68)	93.8(10)	O(4)-W(12)-O(38)	102.5(10)
O(8)-W(10)-O(69)	91.3(9)	O(66)-W(11)-O(20)	95.5(10)	O(4)-W(12)-O(43)	98.7(10)
O(8)-W(10)-O(26)	162.1(8)	O(66)-W(11)-O(65)	164.0(9)	O(4)-W(12)-O(6)	168.8(9)
O(54)-W(13)-O(39)	103.3(11)	O(1)-W(14)-O(47)	105.4(11)	O(11)-W(15)-O(16)	104.6(10)
O(54)-W(13)-O(18)	98.1(9)	O(1)-W(14)-O(36)	100.8(10)	O(11)-W(15)-O(40)	89.8(9)
O(54)-W(13)-O(58)	102.2(10)	O(1)-W(14)-O(57)	98.9(10)	O(11)-W(15)-O(51)	93.0(9)
O(54)-W(13)-O(25)	96.5(10)	O(1)-W(14)-O(10)	97.5(10)	O(11)-W(15)-O(56)	161.6(9)
O(54)-W(13)-O(26)	166.1(9)	O(1)-W(14)-O(6)	166.1(9)	O(11)-W(15)-O(7)	89.5(9)
O(44)-W(16)-O(20)	103.1(11)	O(35)-W(17)-O(32)	100.2(9)	O(42)-W(18)-O(37)	103.5(10)
O(44)-W(16)-O(12)	102.5(10)	O(35)-W(17)-O(56)	99.8(10)	O(42)-W(18)-O(23)	101.6(10)
O(44)-W(16)-O(38)	101.3(12)	O(35)-W(17)-O(55)	102.3(9)	O(42)-W(18)-O(51)	99.8(10)
O(44)-W(16)-O(13)	95.8(10)	O(35)-W(17)-O(59)	101.1(10)	O(42)-W(18)-O(32)	94.8(9)
O(44)-W(16)-O(65)	169.9(10)	O(35)-W(17)-O(7)	173.5(8)	O(42)-W(18)-O(7)	164.8(10)
O(3)-W(19)-O(69)	99.6(11)	O(27)-Ce(2)-O(39)	76.5(7)	O(27)-Ce(1)-O(24)	96.5(7)
O(3)-W(19)-O(25)	104.5(12)	O(27)-Ce(2)-O(3W)	151.3(8)	O(27)-Ce(1)-O(47)	94.3(7)
O(3)-W(19)-O(12)	101.0(10)	O(27)-Ce(2)-O(11)	81.3(7)	O(27)-Ce(1)-O(4W)	81.2(8)
O(3)-W(19)-O(14)	99.8(12)	O(27)-Ce(2)-O(53)	126.9(7)	O(27)-Ce(1)-O(37)	65.4(6)
O(3)-W(19)-O(26)	173.7(9)	O(27)-Ce(2)-O(49)	123.4(7)	O(27)-Ce(1)-O(34)	66.2(7)
O(26)-As(1)-O(65)	98.5(9)	O(27)-Ce(2)-O(19)	70.6(7)	O(27)-Ce(1)-O(8A)	132.6(7)
O(26)-As(1)-O(6)	95.8(9)	O(27)-Ce(2)-O(5W)	82.5(8)	O(27)-Ce(1)-O(2W)	132.7(7)
O(64)-As(2)-O(7)	99.4(10)	O(64)-As(2)-O(28)	95.5(10)	O(27)-Ce(1)-O(1W)	153.5(7)

Symmetry transformations used to generate equivalent atoms: A: -x,-y+2,-z

Table S2. Selected bond lengths (Å) and bond angles(º)of **2**

W(1)-O(62)	1.76(2)	W(2)-O(37)	1.69(2)	W(3)-O(43)	1.73(3)
W(1)-O(59)	1.80(2)	W(2)-O(48)	1.85(2)	W(3)-O(25)	1.89(2)
W(1)-O(79A)	1.94(2)	W(2)-O(51)	1.87(2)	W(3)-O(14)	1.90(2)
W(1)-O(20)	1.95(3)	W(2)-O(66)	1.92(2)	W(3)-O(12)	1.92(2)
W(1)-O(33A)	2.02(2)	W(2)-O(75)	1.97(2)	W(3)-O(42)	1.97(3)
W(1)-O(11)	2.22(2)	W(2)-O(7)	2.28(2)	W(3)-O(17)	2.35(2)
W(4)-O(47)	1.70(2)	W(5)-O(22)	1.74(2)	W(6)-O(21)	1.74(3)
W(4)-O(4)	1.79(2)	W(5)-O(74)	1.78(2)	W(6)-O(2)	1.79(2)
W(4)-O(26)	1.89(2)	W(5)-O(25)	1.95(2)	W(6)-O(61)	1.88(3)
W(4)-O(64)	1.99(2)	W(5)-O(51)	1.96(3)	W(6)-O(14)	1.96(2)
W(4)-O(48)	2.01(2)	W(5)-O(2)	2.11(2)	W(6)-O(49)	2.01(3)
W(4)-O(13)	2.42(2)	W(5)-O(4)	2.12(2)	W(6)-O(10)	2.35(2)
W(7)-O(34)	1.71(3)	W(8)-O(71)	1.66(3)	W(9)-O(30)	1.74(2)
W(7)-O(65)	1.75(2)	W(8)-O(79)	1.89(2)	W(9)-O(46)	1.88(3)
W(7)-O(45)	1.83(3)	W(8)-O(76)	1.90(2)	W(9)-O(36)	1.90(2)
W(7)-O(20)	1.88(2)	W(8)-O(75)	1.91(2)	W(9)-O(42)	1.93(2)
W(7)-O(57)	2.00(2)	W(8)-O(39)	1.95(2)	W(9)-O(45)	1.98(3)
W(7)-O(19)	2.23(2)	W(8)-O(7)	2.35(2)	W(9)-O(17)	2.31(2)
W(10)-O(58)	1.68(3)	W(11)-O(63)	1.69(3)	W(12)-O(54)	1.74(3)
W(10)-O(57)	1.83(2)	W(11)-O(33)	1.83(2)	W(12)-O(16)	1.83(3)
W(10)-O(36)	1.93(3)	W(11)-O(39)	1.87(2)	W(12)-O(49)	1.88(3)
W(10)-O(27)	1.96(3)	W(11)-O(23)	1.89(3)	W(12)-O(24)	1.90(3)
W(10)-O(68)	1.97(2)	W(11)-O(53)	1.92(3)	W(12)-O(15)	2.05(3)
W(10)-O(31)	2.42(2)	W(11)-O(5)	2.45(3)	W(12)-O(10)	2.33(2)
W(13)-O(50)	1.70(3)	W(14)-O(67)	1.66(3)	W(15)-O(32)	1.68(3)
W(13)-O(6)	1.85(2)	W(14)-O(15)	1.80(3)	W(15)-O(64)	1.86(3)
W(13)-O(52)	1.87(3)	W(14)-O(44)	1.87(3)	W(15)-O(3)	1.89(3)
W(13)-O(66)	1.96(2)	W(14)-O(12)	1.97(2)	W(15)-O(1)	1.97(3)
W(13)-O(76)	1.99(2)	W(14)-O(46)	1.98(3)	W(15)-O(52)	1.98(3)
W(13)-O(7)	2.33(2)	W(14)-O(17)	2.33(2)	W(15)-O(13)	2.35(2)
W(16)-O(18)	1.70(2)	W(17)-O(28)	1.73(2)	W(18)-O(72)	1.69(3)
W(16)-O(56)	1.71(3)	W(17)-O(60)	1.76(3)	W(18)-O(69)	1.82(3)
W(16)-O(8)	1.89(3)	W(17)-O(9)	1.93(2)	W(18)-O(24)	1.91(3)
W(16)-O(68)	1.94(2)	W(17)-O(26)	1.97(2)	W(18)-O(27)	1.94(3)
W(16)-O(69)	2.06(3)	W(17)-O(3)	2.11(2)	W(18)-O(44)	1.97(3)
W(16)-O(31)	2.29(3)	W(17)-O(13)	2.23(2)	W(18)-O(31)	2.36(3)
W(19)-O(41)	1.74(2)	W(20)-O(70)	1.66(2)	W(21)-O(38)	1.73(2)
W(19)-O(35)	1.75(3)	W(20)-O(40)	1.78(2)	W(21)-O(1)	1.84(3)
W(19)-O(8)	1.93(3)	W(20)-O(9)	1.93(3)	W(21)-O(29)	1.85(3)
W(19)-O(61)	1.96(3)	W(20)-O(53)	1.94(3)	W(21)-O(23)	1.93(3)
W(19)-O(16)	2.11(3)	W(20)-O(29)	2.04(3)	W(21)-O(6)	2.00(3)
W(19)-O(10)	2.29(2)	W(20)-O(5)	2.25(2)	W(21)-O(5)	2.36(2)
W(22)-O(73)	1.78(3)	Ce(1)-O(80)	2.41(3)	Ce(2)-O(77A)	2.37(3)

W(22)-O(77)	1.81(3)	Ce(1)-O(62A)	2.44(2)	Ce(2)-O(5W)	2.401(10)
W(22)-O(78)	1.97(4)	Ce(1)-O(73)	2.45(3)	Ce(2)-O(5AW)	2.403(10)
W(22)-O(55)	2.001(3)	Ce(1)-O(60)	2.47(3)	Ce(2)-O(34)	2.46(3)
W(22)-O(59)	2.06(2)	Ce(1)-O(74)	2.47(2)	Ce(2)-O(35)	2.47(3)
W(22)-O(65)	2.13(2)	Ce(1)-O(1W)	2.50(4)	Ce(2)-O(22)	2.49(2)
As(1)-O(7)	1.79(2)	Ce(1)-O(40)	2.53(2)	Ce(2)-O(81)	2.56(4)
As(1)-O(13)	1.80(2)	Ce(1)-O(2W)	2.62(4)	Ce(2)-O(18)	2.57(2)
As(1)-O(5)	1.81(2)	Ce(1)-O(3W)	2.65(3)	Ce(2)-O(4W)	2.62(3)
As(2)-O(17)	1.77(2)	As(2)-O(31)	1.80(2)	As(2)-O(10)	1.84(2)
O(62)-W(1)-O(59)	103.0(12)	O(37)-W(2)-O(48)	101.7(11)	O(43)-W(3)-O(25)	105.3(11)
O(62)-W(1)-O(79A)	100.4(11)	O(37)-W(2)-O(51)	103.8(11)	O(43)-W(3)-O(14)	103.6(11)
O(62)-W(1)-O(20)	99.9(11)	O(37)-W(2)-O(66)	100.6(11)	O(43)-W(3)-O(12)	97.2(11)
O(62)-W(1)-O(33A)	91.0(10)	O(37)-W(2)-O(75)	97.5(10)	O(43)-W(3)-O(42)	97.2(12)
O(62)-W(1)-O(11)	169.1(10)	O(37)-W(2)-O(7)	168.1(10)	O(43)-W(3)-O(17)	166.2(11)
O(47)-W(4)-O(4)	103.4(11)	O(22)-W(5)-O(74)	102.5(10)	O(21)-W(6)-O(2)	103.9(11)
O(47)-W(4)-O(26)	101.9(12)	O(22)-W(5)-O(25)	97.3(10)	O(21)-W(6)-O(61)	100.0(12)
O(47)-W(4)-O(64)	95.2(12)	O(22)-W(5)-O(51)	99.0(10)	O(21)-W(6)-O(14)	103.7(10)
O(47)-W(4)-O(48)	101.4(11)	O(22)-W(5)-O(2)	88.7(8)	O(21)-W(6)-O(49)	92.5(12)
O(47)-W(4)-O(13)	164.8(10)	O(22)-W(5)-O(4)	168.9(9)	O(21)-W(6)-O(10)	162.5(10)
O(34)-W(7)-O(65)	100.6(13)	O(71)-W(8)-O(79)	105.3(12)	O(30)-W(9)-O(46)	102.9(11)
O(34)-W(7)-O(45)	103.9(12)	O(71)-W(8)-O(76)	97.9(12)	O(30)-W(9)-O(36)	99.2(12)
O(34)-W(7)-O(20)	97.6(12)	O(71)-W(8)-O(75)	100.3(11)	O(30)-W(9)-O(42)	98.6(11)
O(34)-W(7)-O(57)	91.8(12)	O(71)-W(8)-O(39)	100.6(12)	O(30)-W(9)-O(45)	99.6(11)
O(34)-W(7)-O(19)	171.1(11)	O(71)-W(8)-O(7)	168.8(11)	O(30)-W(9)-O(17)	172.1(10)
O(58)-W(10)-O(57)	102.5(13)	O(63)-W(11)-O(33)	103.2(12)	O(54)-W(12)-O(16)	101.9(13)
O(58)-W(10)-O(36)	100.5(14)	O(63)-W(11)-O(39)	101.7(13)	O(54)-W(12)-O(49)	101.5(13)
O(58)-W(10)-O(27)	94.9(12)	O(63)-W(11)-O(23)	94.2(13)	O(54)-W(12)-O(24)	100.1(13)
O(58)-W(10)-O(68)	104.3(13)	O(63)-W(11)-O(53)	105.9(13)	O(54)-W(12)-O(15)	98.6(12)
O(58)-W(10)-O(31)	167.0(11)	O(63)-W(11)-O(5)	165.3(11)	O(54)-W(12)-O(10)	174.5(11)
O(50)-W(13)-O(6)	103.8(13)	O(67)-W(14)-O(15)	99.2(14)	O(32)-W(15)-O(64)	101.7(12)
O(50)-W(13)-O(52)	102.4(13)	O(67)-W(14)-O(44)	100.3(14)	O(32)-W(15)-O(3)	99.6(12)
O(50)-W(13)-O(66)	96.1(13)	O(67)-W(14)-O(12)	100.2(13)	O(32)-W(15)-O(1)	100.3(12)
O(50)-W(13)-O(76)	97.7(13)	O(67)-W(14)-O(46)	99.9(14)	O(32)-W(15)-O(52)	100.2(12)
O(50)-W(13)-O(7)	165.2(12)	O(67)-W(14)-O(17)	169.9(11)	O(32)-W(15)-O(13)	173.4(11)
O(18)-W(16)-O(56)	107.0(14)	O(28)-W(17)-O(60)	102.2(12)	O(72)-W(18)-O(69)	102.2(15)
O(18)-W(16)-O(8)	91.8(12)	O(28)-W(17)-O(9)	100.5(10)	O(72)-W(18)-O(24)	101.6(14)
O(18)-W(16)-O(68)	96.0(11)	O(28)-W(17)-O(26)	95.9(10)	O(72)-W(18)-O(27)	99.4(13)
O(18)-W(16)-O(69)	157.7(12)	O(28)-W(17)-O(3)	94.7(12)	O(72)-W(18)-O(44)	100.8(14)
O(18)-W(16)-O(31)	86.6(10)	O(28)-W(17)-O(13)	166.0(11)	O(72)-W(18)-O(31)	172.3(12)
O(41)-W(19)-O(35)	106.6(13)	O(70)-W(20)-O(40)	107.8(13)	O(38)-W(21)-O(1)	100.8(12)
O(41)-W(19)-O(8)	103.6(13)	O(70)-W(20)-O(9)	100.3(13)	O(38)-W(21)-O(29)	102.1(12)
O(41)-W(19)-O(61)	95.8(12)	O(70)-W(20)-O(53)	96.4(13)	O(38)-W(21)-O(23)	100.8(12)

O(41)-W(19)-O(16)	93.3(12)	O(70)-W(20)-O(29)	94.5(12)	O(38)-W(21)-O(6)	100.7(11)
O(41)-W(19)-O(10)	161.7(11)	O(70)-W(20)-O(5)	164.2(11)	O(38)-W(21)-O(5)	171.8(11)
O(73)-W(22)-O(77)	105.0(12)	O(80)-Ce(1)-O(62A)	79.7(10)	O(77A)-Ce(2)-O(5W)	95.0(3)
O(73)-W(22)-O(78)	89.6(14)	O(80)-Ce(1)-O(73)	73.0(9)	O(77A)-Ce(2)-O(5AW)	115.0(2)
O(73)-W(22)-O(55)	95.3(9)	O(80)-Ce(1)-O(60)	132.1(10)	O(77A)-Ce(2)-O(34)	70.3(11)
O(73)-W(22)-O(59)	165.2(11)	O(80)-Ce(1)-O(74)	139.1(10)	O(77A)-Ce(2)-O(35)	155.0(9)
O(73)-W(22)-O(65)	88.3(10)	O(80)-Ce(1)-O(1W)	76.3(12)	O(77A)-Ce(2)-O(22)	78.0(9)
		O(80)-Ce(1)-O(40)	74.0(10)	O(77A)-Ce(2)-O(81)	70.6(11)
		O(80)-Ce(1)-O(2W)	71.3(11)	O(77A)-Ce(2)-O(18)	136.3(9)
		O(80)-Ce(1)-O(3W)	133.2(11)	O(77A)-Ce(2)-O(4W)	81.2(11)

Symmetry transformations used to generate equivalent atoms: A: -x+1,-y+1,-z+1

Table S3. Selected bond lengths (Å) and bond angles (º)of **3**

W(1)-O(119)	1.76(3)	W(2)-O(112)	1.74(2)	W(3)-O(124)	1.69(3)
W(1)-O(63)	1.77(2)	W(2)-O(50)	1.78(2)	W(3)-O(89)	1.91(3)
W(1)-O(42)	1.84(3)	W(2)-O(43)	1.85(3)	W(3)-O(38)	1.92(3)
W(1)-O(60)	1.88(3)	W(2)-O(89)	1.96(2)	W(3)-O(135)	1.92(3)
W(1)-O(132)	2.05(3)	W(2)-O(80)	2.00(3)	W(3)-O(115)	1.93(3)
W(1)-O(74)	2.29(3)			W(3)-O(47)	2.28(3)
W(4)-O(49)	1.77(3)	W(5)-O(86)	1.75(3)	W(6)-O(97)	1.76(4)
W(4)-O(38)	1.88(3)	W(5)-O(127)	1.80(2)	W(6)-O(54)	1.77(3)
W(4)-O(80)	1.88(3)	W(5)-O(134)	1.89(3)	W(6)-O(134)	1.94(3)
W(4)-O(75)	1.95(3)	W(5)-O(79)	1.95(3)	W(6)-O(101)	1.95(3)
W(4)-O(120)	1.96(3)	W(5)-O(56)	2.00(3)	W(6)-O(11)	1.98(3)
W(4)-O(67)	2.33(3)	W(5)-O(57)	2.34(3)	W(6)-O(2)	2.37(4)
W(7)-O(81)	1.69(3)	W(8)-O(99)	1.78(3)	W(9)-O(95)	1.72(3)
W(7)-O(64)	1.75(2)	W(8)-O(53)	1.87(2)	W(9)-O(68)	1.79(3)
W(7)-O(90)	1.89(3)	W(8)-O(39)	1.88(2)	W(9)-O(120)	1.94(3)
W(7)-O(60)	1.99(3)	W(8)-O(37)	1.91(2)	W(9)-O(42)	1.98(3)
W(7)-O(94)	2.10(3)	W(8)-O(36)	1.95(3)	W(9)-O(84)	2.06(3)
W(7)-O(74)	2.30(3)			W(9)-O(67)	2.32(3)
W(10)-O(9)	1.72(3)	W(11)-O(116)	1.76(3)	W(12)-O(55)	1.75(3)
W(10)-O(94)	1.79(3)	W(11)-O(144)	1.77(3)	W(12)-O(52)	1.79(3)
W(10)-O(132)	1.88(3)	W(11)-O(90)	1.93(3)	W(12)-O(71)	1.91(3)
W(10)-O(98)	1.89(2)	W(11)-O(115)	1.96(3)	W(12)-O(82)	1.94(3)
W(10)-O(118)	1.95(3)	W(11)-O(65)	1.96(3)	W(12)-O(140)	2.02(3)
W(10)-O(74)	2.42(3)	W(11)-O(47)	2.40(3)	W(12)-O(41)	2.37(3)
W(13)-O(27)	1.73(3)	W(14)-O(6)	1.76(3)	W(15)-O(138)	1.70(3)
W(13)-O(70)	1.83(3)	W(14)-O(105)	1.77(2)	W(15)-O(88)	1.74(3)
W(13)-O(87)	1.83(3)	W(14)-O(131)	1.94(3)	W(15)-O(136)	1.87(4)
W(13)-O(91)	1.97(3)	W(14)-O(59)	1.94(3)	W(15)-O(79)	1.97(3)
W(13)-O(130)	2.01(3)	W(14)-O(15)	2.08(3)	W(15)-O(10)	2.03(3)

		W(14)-O(93)	2.27(3)	W(15)-O(57)	2.34(3)
W(16)-O(40)	1.65(4)	W(17)-O(141)	1.75(3)	W(18)-O(110)	1.72(3)
W(16)-O(147)	1.89(3)	W(17)-O(118)	1.87(3)	W(18)-O(48)	1.79(3)
W(16)-O(65)	1.91(3)	W(17)-O(84)	1.89(3)	W(18)-O(71)	1.90(3)
W(16)-O(98)	1.95(2)	W(17)-O(147)	1.95(3)	W(18)-O(14)	2.00(3)
W(16)-O(135)	1.99(3)	W(17)-O(75)	1.96(3)	W(18)-O(22)	2.03(3)
W(16)-O(47)	2.34(3)	W(17)-O(67)	2.37(3)	W(18)-O(92)	2.32(3)
W(19)-O(106)	1.81(3)	W(20)-O(123)	1.76(4)	W(21)-O(66)	1.72(3)
W(19)-O(72)	1.81(3)	W(20)-O(76)	1.79(3)	W(21)-O(25)	1.82(4)
W(19)-O(73)	1.83(3)	W(20)-O(142)	1.90(3)	W(21)-O(129)	1.98(3)
W(19)-O(102)	1.99(3)	W(20)-O(126)	1.96(4)	W(21)-O(35)	1.99(3)
W(19)-O(13)	2.02(3)	W(20)-O(21)	2.08(4)	W(21)-O(108)	2.03(3)
		W(20)-O(100)	2.38(3)	W(21)-O(122)	2.33(4)
W(22)-O(29)	1.77(4)	W(23)-O(109)	1.74(3)	W(24)-O(77)	1.75(3)
W(22)-O(44)	1.87(4)	W(23)-O(51)	1.83(3)	W(24)-O(20)	1.76(3)
W(22)-O(130)	1.87(3)	W(23)-O(59)	1.87(3)	W(24)-O(69)	1.78(3)
W(22)-O(30)	1.91(3)	W(23)-O(85)	1.94(3)	W(24)-O(139)	1.99(3)
W(22)-O(101)	1.93(3)	W(23)-O(111)	2.03(3)	W(24)-O(17)	2.03(3)
W(22)-O(2)	2.32(3)	W(23)-O(8)	2.36(3)		
W(25)-O(148)	1.68(4)	W(26)-O(34)	1.68(4)	W(27)-O(121)	1.70(3)
W(25)-O(46)	1.71(3)	W(26)-O(140)	1.81(4)	W(27)-O(113)	1.82(3)
W(25)-O(102)	1.90(3)	W(26)-O(78)	1.91(4)	W(27)-O(35)	1.83(3)
W(25)-O(5)	1.92(4)	W(26)-O(107)	1.93(3)	W(27)-O(14)	1.91(3)
W(25)-O(129)	1.94(3)	W(26)-O(45)	2.07(3)	W(27)-O(146)	2.00(3)
W(25)-O(122)	2.33(3)	W(26)-O(41)	2.37(2)	W(27)-O(92)	2.42(3)
W(28)-O(104)	1.75(3)	W(29)-O(7)	1.70(4)	W(30)-O(33)	1.67(4)
W(28)-O(83)	1.79(3)	W(29)-O(62)	1.78(2)	W(30)-O(96)	1.82(3)
W(28)-O(117)	1.95(3)	W(29)-O(142)	1.93(3)	W(30)-O(15)	1.87(3)
W(28)-O(136)	1.97(3)	W(29)-O(131)	1.94(3)	W(30)-O(18)	1.97(4)
W(28)-O(133)	2.06(3)	W(29)-O(96)	2.05(3)	W(30)-O(143)	1.98(3)
W(28)-O(12)	2.33(3)	W(29)-O(93)	2.32(3)	W(30)-O(93)	2.41(3)
W(31)-O(149)	1.77(4)	W(32)-O(1)	1.67(3)	W(33)-O(125)	1.70(4)
W(31)-O(22)	1.82(4)	W(32)-O(13)	1.84(3)	W(33)-O(139)	1.85(3)
W(31)-O(146)	1.83(3)	W(32)-O(82)	1.98(3)	W(33)-O(32)	1.85(3)
W(31)-O(4)	1.88(4)	W(32)-O(107)	1.99(3)	W(33)-O(85)	1.91(3)
W(31)-O(78)	1.99(4)	W(32)-O(46)	2.10(3)	W(33)-O(16)	1.95(3)
W(31)-O(92)	2.46(3)	W(32)-O(41)	2.50(2)	W(33)-O(8)	2.30(3)
W(34)-O(31)	1.82(4)	W(35)-O(28)	1.81(4)	W(36)-O(24)	1.68(3)
W(34)-O(133)	1.88(3)	W(35)-O(21)	1.82(3)	W(36)-O(103)	1.93(3)
W(34)-O(91)	1.90(3)	W(35)-O(18)	1.86(4)	W(36)-O(11)	1.93(4)
W(34)-O(26)	1.94(3)	W(35)-O(23)	1.93(3)	W(36)-O(61)	1.93(4)
W(34)-O(44)	1.97(4)	W(35)-O(114)	2.04(4)	W(36)-O(30)	1.95(3)
W(34)-O(12)	2.43(3)	W(35)-O(100)	2.34(3)	W(36)-O(2)	2.35(3)

W(37)-O(145)	1.70(4)	W(38)-O(3)	1.77(4)	W(39)-O(19)	1.74(4)
W(37)-O(17)	1.85(3)	W(38)-O(10)	1.91(3)	W(39)-O(143)	1.88(3)
W(37)-O(114)	1.86(4)	W(38)-O(103)	1.92(3)	W(39)-O(111)	1.89(3)
W(37)-O(126)	1.91(3)	W(38)-O(56)	1.93(3)	W(39)-O(23)	1.95(3)
W(37)-O(32)	1.97(3)	W(38)-O(128)	1.97(4)	W(39)-O(16)	1.98(3)
W(37)-O(100)	2.31(3)	W(38)-O(57)	2.36(3)	W(39)-O(8)	2.38(3)
W(40)-O(45)	1.73(3)	W(41)-O(137)	1.68(4)	Ce(1)-O(43)	2.24(3)
W(40)-O(58)	1.81(4)	W(41)-O(128)	1.85(4)	Ce(1)-O(87)	2.25(3)
W(40)-O(108)	1.82(3)	W(41)-O(61)	1.88(4)	Ce(1)-O(54)	2.31(3)
W(40)-O(5)	1.92(4)	W(41)-O(117)	1.91(3)	Ce(1)-O(68)	2.32(3)
W(40)-O(4)	1.95(3)	W(41)-O(26)	1.95(3)	Ce(1)-O(37)	2.35(2)
W(40)-O(122)	2.36(3)	W(41)-O(12)	2.35(3)	Ce(1)-O(127)	2.36(3)
Ce(2)-O(73)	2.28(3)	Ce(3)-O(51)	2.28(3)	Ce(1)-O(63)	2.40(2)
Ce(2)-O(50)	2.30(2)	Ce(3)-O(72)	2.30(3)	Ce(1)-O(39)	2.41(3)
Ce(2)-O(48)	2.31(3)	Ce(3)-O(113)	2.30(3)	Ce(4)-O(69)	2.29(3)
Ce(2)-O(52)	2.31(3)	Ce(3)-O(77)	2.35(3)	Ce(4)-O(70)	2.31(3)
Ce(2)-O(144)	2.35(3)	Ce(3)-O(36)	2.35(2)	Ce(4)-O(76)	2.32(3)
Ce(2)-O(37)	2.42(2)	Ce(3)-O(66)	2.36(3)	Ce(4)-O(104)	2.35(3)
Ce(2)-O(53)	2.45(3)	Ce(3)-O(105)	2.39(2)	Ce(4)-O(88)	2.39(3)
Ce(2)-O(64)	2.46(2)	Ce(3)-O(53)	2.43(3)	Ce(4)-O(62)	2.40(2)
As(1)-O(67)	1.77(3)	As(2)-O(41)	1.65(3)	Ce(4)-O(36)	2.41(2)
As(1)-O(47)	1.79(3)	As(2)-O(92)	1.69(3)	Ce(4)-O(39)	2.46(3)
As(1)-O(74)	1.81(3)	As(2)-O(122)	1.75(4)	As(3)-O(12)	1.72(3)
As(4)-O(8)	1.76(3)	As(4)-O(100)	1.76(3)	As(3)-O(2)	1.75(3)
As(4)-O(93)	1.83(3)			As(3)-O(57)	1.78(3)
O(119)-Mn(1)	2.16(2)	Mn(1)-O(1W)	2.21(3)	Mn(1)-O(2WA)	2.31(4)
Mn(1)-O(119A)	2.16(2)	Mn(1)-O(1WA)	2.21(3)	Mn(1)-O(2W)	2.31(4)
O(119)-W(1)-O(63)	103.3(12)	O(112)-W(2)-O(50)	105.6(12)	O(124)-W(3)-O(89)	102.6(14)
O(119)-W(1)-O(42)	101.9(12)	O(112)-W(2)-O(43)	103.7(12)	O(124)-W(3)-O(38)	102.0(13)
O(119)-W(1)-O(60)	96.6(12)	O(112)-W(2)-O(89)	102.8(11)	O(124)-W(3)-O(135)	99.5(15)
O(119)-W(1)-O(132)	92.2(12)	O(112)-W(2)-O(80)	100.4(11)	O(124)-W(3)-O(115)	99.9(14)
O(119)-W(1)-O(74)	162.0(11)			O(124)-W(3)-O(47)	172.8(13)
O(49)-W(4)-O(38)	102.0(12)	O(86)-W(5)-O(127)	102.0(13)	O(97)-W(6)-O(54)	105.2(14)
O(49)-W(4)-O(80)	101.8(12)	O(86)-W(5)-O(134)	102.5(14)	O(97)-W(6)-O(134)	103.3(14)
O(49)-W(4)-O(75)	101.2(12)	O(86)-W(5)-O(79)	98.2(13)	O(97)-W(6)-O(101)	98.8(14)
O(49)-W(4)-O(120)	99.2(12)	O(86)-W(5)-O(56)	97.0(13)	O(97)-W(6)-O(11)	94.9(15)
O(49)-W(4)-O(67)	171.3(10)	O(86)-W(5)-O(57)	167.3(12)	O(97)-W(6)-O(2)	165.3(13)
O(81)-W(7)-O(64)	100.4(12)	O(99)-W(8)-O(53)	102.5(11)	O(95)-W(9)-O(68)	105.3(14)
O(81)-W(7)-O(90)	104.7(13)	O(99)-W(8)-O(39)	100.1(11)	O(95)-W(9)-O(120)	98.1(13)
O(81)-W(7)-O(60)	99.0(12)	O(99)-W(8)-O(37)	111.5(12)	O(95)-W(9)-O(42)	103.1(12)
O(81)-W(7)-O(94)	97.6(13)	O(99)-W(8)-O(36)	113.4(12)	O(95)-W(9)-O(84)	94.5(13)
O(81)-W(7)-O(74)	164.3(11)			O(95)-W(9)-O(67)	164.7(13)

O(94)-W(10)-O(132)	93.1(13)	O(116)-W(11)-O(144)	104.9(14)	O(55)-W(12)-O(52)	105.0(13)
O(9)-W(10)-O(98)	101.9(13)	O(116)-W(11)-O(90)	106.0(12)	O(55)-W(12)-O(71)	100.2(13)
O(94)-W(10)-O(98)	86.0(12)	O(116)-W(11)-O(115)	95.2(13)	O(55)-W(12)-O(82)	100.9(12)
O(94)-W(10)-O(118)	156.5(12)	O(116)-W(11)-O(65)	97.0(13)	O(55)-W(12)-O(140)	98.8(14)
O(94)-W(10)-O(74)	72.7(11)	O(116)-W(11)-O(47)	163.3(13)	O(55)-W(12)-O(41)	168.8(10)
O(27)-W(13)-O(70)	104.3(13)	O(6)-W(14)-O(105)	100.3(13)	O(138)-W(15)-O(88)	104.5(14)
O(27)-W(13)-O(87)	105.4(14)	O(6)-W(14)-O(131)	101.8(13)	O(138)-W(15)-O(136)	100.0(16)
O(27)-W(13)-O(91)	101.0(13)	O(6)-W(14)-O(59)	99.7(14)	O(138)-W(15)-O(79)	100.5(15)
O(27)-W(13)-O(130)	101.4(12)	O(6)-W(14)-O(15)	94.3(14)	O(138)-W(15)-O(10)	96.1(14)
		O(6)-W(14)-O(93)	165.8(12)	O(138)-W(15)-O(57)	167.5(13)
O(40)-W(16)-O(147)	101.0(14)	O(141)-W(17)-O(118)	103.3(13)	O(110)-W(18)-O(48)	104.9(13)
O(40)-W(16)-O(65)	102.9(14)	O(141)-W(17)-O(84)	101.4(13)	O(110)-W(18)-O(71)	102.7(15)
O(40)-W(16)-O(98)	99.8(13)	O(141)-W(17)-O(147)	99.6(14)	O(110)-W(18)-O(14)	98.4(14)
O(40)-W(16)-O(135)	101.2(14)	O(141)-W(17)-O(75)	96.6(13)	O(110)-W(18)-O(22)	96.6(14)
O(40)-W(16)-O(47)	171.9(12)	O(141)-W(17)-O(67)	168.7(12)	O(110)-W(18)-O(92)	167.1(12)
O(106)-W(19)-O(72)	102.8(13)	O(123)-W(20)-O(76)	105.1(15)	O(66)-W(21)-O(25)	107.1(15)
O(106)-W(19)-O(73)	106.0(13)	O(123)-W(20)-O(142)	101.6(16)	O(66)-W(21)-O(129)	90.3(12)
O(106)-W(19)-O(102)	100.9(13)	O(123)-W(20)-O(126)	99.9(16)	O(66)-W(21)-O(35)	91.5(13)
O(106)-W(19)-O(13)	104.9(13)	O(123)-W(20)-O(21)	96.5(15)	O(66)-W(21)-O(108)	156.6(13)
		O(123)-W(20)-O(100)	165.0(15)	O(66)-W(21)-O(122)	86.6(12)
O(29)-W(22)-O(44)	106.9(18)	O(109)-W(23)-O(51)	103.9(13)	O(77)-W(24)-O(20)	105.2(14)
O(29)-W(22)-O(130)	100.9(14)	O(109)-W(23)-O(59)	101.3(14)	O(77)-W(24)-O(69)	95.2(13)
O(29)-W(22)-O(30)	102.6(15)	O(109)-W(23)-O(85)	101.1(14)	O(77)-W(24)-O(139)	85.6(12)
O(29)-W(22)-O(101)	93.2(16)	O(109)-W(23)-O(111)	96.9(13)	O(77)-W(24)-O(17)	152.5(13)
O(29)-W(22)-O(2)	166.8(16)	O(109)-W(23)-O(8)	167.3(14)		
O(148)-W(25)-O(46)	99.1(15)	O(34)-W(26)-O(140)	100.4(18)	O(121)-W(27)-O(113)	107.3(14)
O(148)-W(25)-O(102)	106.0(14)	O(34)-W(26)-O(78)	100.1(17)	O(121)-W(27)-O(35)	103.1(15)
O(148)-W(25)-O(5)	99.1(17)	O(34)-W(26)-O(107)	97.7(16)	O(121)-W(27)-O(14)	97.9(15)
O(148)-W(25)-O(129)	98.9(16)	O(34)-W(26)-O(45)	101.0(16)	O(121)-W(27)-O(146)	98.7(14)
O(148)-W(25)-O(122)	169.4(14)	O(34)-W(26)-O(41)	173.0(16)	O(121)-W(27)-O(92)	166.7(14)
O(104)-W(28)-O(83)	105.8(13)	O(7)-W(29)-O(62)	101.8(14)	O(33)-W(30)-O(96)	101.9(16)
O(104)-W(28)-O(117)	156.0(14)	O(7)-W(29)-O(142)	102.6(15)	O(33)-W(30)-O(15)	102.1(17)
O(104)-W(28)-O(136)	90.5(13)	O(7)-W(29)-O(131)	97.6(15)	O(33)-W(30)-O(18)	100.2(17)
O(104)-W(28)-O(133)	91.2(12)	O(7)-W(29)-O(96)	96.4(15)	O(33)-W(30)-O(143)	100.6(16)
O(104)-W(28)-O(12)	84.9(12)	O(7)-W(29)-O(93)	163.3(13)	O(33)-W(30)-O(93)	172.2(16)
O(149)-W(31)-O(22)	99.0(19)	O(1)-W(32)-O(13)	108.7(15)	O(125)-W(33)-O(139)	103.9(15)
O(149)-W(31)-O(146)	103.1(17)	O(1)-W(32)-O(82)	98.8(15)	O(125)-W(33)-O(32)	99.7(17)
O(146)-W(31)-O(4)	86.9(15)	O(1)-W(32)-O(107)	95.3(15)	O(125)-W(33)-O(85)	101.7(15)
O(146)-W(31)-O(78)	157.0(15)	O(1)-W(32)-O(46)	103.0(15)	O(125)-W(33)-O(16)	99.8(16)
O(146)-W(31)-O(92)	72.9(12)	O(1)-W(32)-O(41)	167.9(14)	O(125)-W(33)-O(8)	173.7(13)
O(31)-W(34)-O(133)	98.7(17)	O(28)-W(35)-O(21)	100.9(16)	O(24)-W(36)-O(103)	103.0(15)
O(31)-W(34)-O(91)	106.9(14)	O(28)-W(35)-O(18)	104.3(17)	O(24)-W(36)-O(11)	98.6(17)
O(31)-W(34)-O(26)	95.7(15)	O(28)-W(35)-O(23)	98.6(15)	O(24)-W(36)-O(61)	104.0(17)

O(31)-W(34)-O(44)	98.7(17)	O(28)-W(35)-O(114)	97.3(17)	O(24)-W(36)-O(30)	99.3(15)
O(31)-W(34)-O(12)	168.3(15)	O(28)-W(35)-O(100)	169.1(14)	O(24)-W(36)-O(2)	168.4(14)
O(145)-W(37)-O(17)	102.5(16)	O(3)-W(38)-O(10)	98.8(16)	O(19)-W(39)-O(143)	98.7(17)
O(145)-W(37)-O(114)	97.9(18)	O(3)-W(38)-O(103)	100.8(16)	O(19)-W(39)-O(111)	101.6(16)
O(145)-W(37)-O(126)	100.1(16)	O(3)-W(38)-O(56)	102.2(16)	O(19)-W(39)-O(23)	98.7(17)
O(145)-W(37)-O(32)	101.4(16)	O(3)-W(38)-O(128)	98.8(17)	O(19)-W(39)-O(16)	100.1(17)
O(145)-W(37)-O(100)	172.4(14)	O(3)-W(38)-O(57)	172.2(14)	O(19)-W(39)-O(8)	172.2(15)
O(45)-W(40)-O(58)	96.1(18)	O(137)-W(41)-O(128)	102.4(17)	O(43)-Ce(1)-O(87)	78.8(10)
O(45)-W(40)-O(108)	160.4(14)	O(137)-W(41)-O(61)	102.4(16)	O(43)-Ce(1)-O(54)	82.8(9)
O(45)-W(40)-O(5)	88.9(16)	O(137)-W(41)-O(117)	102.6(17)	O(43)-Ce(1)-O(68)	72.9(10)
O(45)-W(40)-O(4)	83.7(15)	O(137)-W(41)-O(26)	99.6(16)	O(43)-Ce(1)-O(37)	77.3(9)
O(45)-W(40)-O(122)	88.4(13)	O(137)-W(41)-O(12)	171.9(16)	O(43)-Ce(1)-O(127)	149.3(10)
O(73)-Ce(2)-O(50)	76.4(9)	O(51)-Ce(3)-O(72)	135.2(10)	O(43)-Ce(1)-O(63)	110.8(9)
O(73)-Ce(2)-O(48)	112.9(10)	O(51)-Ce(3)-O(113)	84.8(10)	O(43)-Ce(1)-O(39)	135.2(9)
O(73)-Ce(2)-O(52)	73.7(10)	O(51)-Ce(3)-O(77)	69.3(10)	O(69)-Ce(4)-O(70)	76.0(10)
O(73)-Ce(2)-O(144)	137.4(9)	O(51)-Ce(3)-O(36)	117.3(9)	O(69)-Ce(4)-O(76)	73.4(10)
O(73)-Ce(2)-O(64)	151.0(9)	O(51)-Ce(3)-O(66)	72.7(9)	O(69)-Ce(4)-O(104)	86.1(10)
O(67)-As(1)-O(47)	97.2(13)	O(51)-Ce(3)-O(105)	70.7(9)	O(69)-Ce(4)-O(88)	148.6(10)
O(67)-As(1)-O(74)	99.0(12)	O(51)-Ce(3)-O(53)	148.1(9)	O(69)-Ce(4)-O(62)	110.9(9)
O(41)-As(2)-O(92)	94.3(14)	O(119)-Mn(1)-O(1W)	91.1(10)	O(69)-Ce(4)-O(36)	75.6(10)
O(41)-As(2)-O(122)	102.4(14)	O(119)-Mn(1)-O(1WA)	88.9(10)	O(69)-Ce(4)-O(39)	133.8(9)
O(12)-As(3)-O(2)	100.2(15)	O(119)-Mn(1)-O(2WA)	85.9(11)		
O(12)-As(3)-O(57)	95.7(15)	O(119)-Mn(1)-O(2W)	94.1(11)		
O(8)-As(4)-O(100)	98.4(14)				
O(8)-As(4)-O(93)	98.6(13)				

Symmetry transformations used to generate equivalent atoms: A: -x+1,-y+2,-z

Table S4 Bond valence sum calculations of Ce, W and As for **1.**

Bonds	Bond length (Å)	BVS*	Bonds	Bond length (Å)	BVS*
Ce(1)-O(27)	2.310(19)	0.78	Ce(1)-O(34)	2.59(2)	0.37
Ce(1)-O(24)	2.48(2)	0.50	Ce(1)-O(8A)	2.59(2)	0.37
Ce(1)-O(47)	2.48(2)	0.50	Ce(1)-O(2W)	2.61(2)	0.35
Ce(1)-O(4W)	2.56(2)	0.40	Ce(1)-O(1W)	2.81(3)	0.20
Ce(1)-O(37)	2.58(2)	0.38			
$\boldsymbol{V_{Ce(1)}}$ **= 3.85**					
Ce(2)-O(27)	2.277(19)	0.86	Ce(2)-O(53)	2.48(2)	0.50
Ce(2)-O(39)	2.43(2)	0.57	Ce(2)-O(49)	2.52(2)	0.44
Ce(2)-O(3W)	2.47(3)	0.51	Ce(2)-O(19)	2.60(2)	0.36
Ce(2)-O(11)	2.48(2)	0.50	Ce(2)-O(5W)	2.68(3)	0.29
$\boldsymbol{V_{Ce(2)}}$ **= 4.03**					
W(2)-O(19)	1.72(2)	1.70	W(2)-O(9)	1.910(17)	1.02
W(2)-O(29)	1.87(2)	1.14	W(2)-O(62)	1.94(2)	0.94

W(2)-O(17)	1.88(2)	1.11	W(2)-O(63)	2.27(2)	0.39
$V_{W(2)}$ = 6.30					
As(1)-O(26)	1.78(2)	1.02	As(2)-O(64)	1.80(2)	0.97
As(1)-O(65)	1.791(19)	0.99	As(2)-O(7)	1.797(19)	0.98
As(1)-O(6)	1.80(2)	0.97	As(2)-O(28)	1.81(2)	0.94
$V_{As(1)}$ = 2.98			**$V_{As(2)}$ = 2.89**		

*$V_M = \sum_j S_{M-O_j} = \sum_j \exp(\frac{r_0 - r_{M-O_j}}{0.37})$; $r_{Ce\text{-}O}$ =2.220 Å; $r_{W\text{-}O}$ =.917 Å; $r_{As\text{-}O}$ =1.789 Å. [1]

[1] Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.

Table S5 Bond valence sum calculations of Ce, W and As for **2**.

Bonds	Bond length (Å)	BVS*	Bonds	Bond length (Å)	BVS*
Ce(1)–O(80)	2.41(3)	0.60	Ce(1)–O(1W)	2.50(4)	0.47
Ce(1)–O(60)	2.47(2)	0.51	Ce(1)–O(40)	2.53(2)	0.43
Ce(1)–O(62A)	2.44(2)	0.55	Ce(1)–O(3W)	2.65(3)	0.31
Ce(1)–O(74)	2.47(2)	0.51	Ce(1)–O(2W)	2.62(4)	0.34
Ce(1)–O(73)	2.45(3)	0.54			
$V_{Ce(1)}$ = 4.26					
Ce(2)–O(77A)	2.37(3)	0.67	Ce(2)–O(22)	2.49(2)	0.48
Ce(2)–O(5W)	2.401(1)	0.61	Ce(2)–O(81)	2.56(4)	0.40
Ce(2)–O(35)	2.47(3)	0.51	Ce(2)–O(18)	2.57(2)	0.39
Ce(2)–O(34)	2.46(3)	0.52	Ce(2)–O(4W)	2.62(3)	0.34
$V_{Ce(2)}$ = 3.92					
W(22)-O(73)	1.78(3)	1.45	W(22)-O(55)	2.001(3)	0.80
W(22)-O(77)	1.81(3)	1.34	W(22)-O(59)	2.06(2)	0.68
W(22)-O(78)	1.97(4)	0.87	W(22)-O(65)	2.13(2)	0.56
$V_{W(22)}$ = 5.70					
As(1)-O(7)	1.79(2)	1.00	As(2)-O(17)	1.77(2)	1.05
As(1)-O(13)	1.80(2)	0.97	As(2)-O(31)	1.80(2)	0.97
As(1)-O(5)	1.81(2)	0.94	As(2)-O(10)	1.84(2)	0.87
$V_{As(1)}$ = 2.91			**$V_{As(2)}$ = 2.89**		

*$V_M = \sum_j S_{M-O_j} = \sum_j \exp(\frac{r_0 - r_{M-O_j}}{0.37})$; $r_{Ce\text{–}O}$ =2.220 Å; $r_{W\text{–}O}$ =1.917 Å; $r_{As\text{–}O}$ =1.789 Å.[22]

Table S6 Bond valence sum calculations of Ce, W, Mn and As for **3**.

Bonds	Bond length (Å)	BVS*	Bonds	Bond length (Å)	BVS
Ce(1)-O(43)	2.24(3)	**0.95/0.65**	Ce(1)-O(37)	2.35(2)	**0.70/0.48**
Ce(1)-O(87)	2.25(3)	**0.92/0.63**	Ce(1)-O(127)	2.36(3)	**0.68/0.47**
Ce(1)-O(54)	2.31(3)	**0.78/0.54**	Ce(1)-O(63)	2.40(2)	**0.61/0.42**
Ce(1)-O(68)	2.32(3)	**0.76/0.52**	Ce(1)-O(39)	2.41(3)	**0.60/0.41**
$V_{Ce(1)}$ = 6.00/4.12					
Ce(2)-O(73)	2.28(3)	**0.85/0.58**	Ce(2)-O(144)	2.35(3)	**0.70/0.48**

Ce(2)-O(50)	2.30(2)	**0.81/0.55**	Ce(2)-O(37)	2.42(2)	**0.58/0.40**
Ce(2)-O(48)	2.31(3)	**0.78/0.54**	Ce(2)-O(53)	2.45(3)	**0.54/0.37**
Ce(2)-O(52)	2.31(3)	**0.78/0.54**	Ce(2)-O(64)	2.46(2)	**0.52/0.36**
$\boldsymbol{V_{Ce(2)}}$ **= 5.56/3.82**					
Ce(3)-O(51)	2.28(3)	**0.85/0.58**	Ce(3)-O(36)	2.35(2)	**0.70/0.48**
Ce(3)-O(72)	2.30(3)	**0.81/0.55**	Ce(3)-O(66)	2.36(3)	**0.68/0.47**
Ce(3)-O(113)	2.30(3)	**0.81/0.55**	Ce(3)-O(105)	2.39(2)	**0.63/0.43**
Ce(3)-O(77)	2.35(3)	**0.70/0.48**	Ce(3)-O(53)	2.43(3)	**0.57/0.39**
$\boldsymbol{V_{Ce(3)}}$ **= 5.75/3.93**					
Ce(4)–O(69)	2.29(3)	**0.83/0.57**	Ce(4)–O(88)	2.39(3)	**0.63/0.43**
Ce(4)–O(70)	2.31(3)	**0.78/0.54**	Ce(4)–O(62)	2.40(2)	**0.61/0.42**
Ce(4)–O(76)	2.32(3)	**0.76/0.52**	Ce(4)–O(36)	2.41(2)	**0.60/0.41**
Ce(4)–O(104)	2.35(3)	**0.70/0.48**	Ce(4)–O(39)	2.46(3)	**0.52/0.36**
$\boldsymbol{V_{Ce(4)}}$ **= 5.43/3.73**					
W(2)-O(112)	1.74(2)	**1.62**	W(2)-O(89)	1.96(2)	**0.89**
W(2)-O(50)	1.78(2)	**1.45**	W(2)-O(80)	2.00(3)	**0.80**
W(2)-O(43)	1.85(3)	**1.20**			
$\boldsymbol{V_{W(2)}}$ **= 5.96**					
W(8)-O(99)	1.78(3)	**1.45**	W(8)-O(37)	1.91(2)	**1.02**
W(8)-O(53)	1.87(2)	**1.14**	W(8)-O(36)	1.95(3)	**0.92**
W(8)-O(39)	1.88(2)	**1.11**			
$\boldsymbol{V_{W(8)}}$ **= 5.64**					
W(13)-O(27)	1.73(3)	**1.66**	W(13)-O(91)	1.97(3)	**0.87**
W(13)-O(70)	1.83(3)	**1.27**	W(13)-O(130)	2.01(3)	**0.78**
W(13)-O(87)	1.83(3)	**1.27**			
$\boldsymbol{V_{W(13)}}$ **= 5.85**					
W(19)-O(106)	1.81(3)	**1.34**	W(19)-O(102)	1.99(3)	**0.84**
W(19)-O(72)	1.81(3)	**1.34**	W(19)-O(13)	2.02(3)	**0.77**
W(19)-O(73)	1.83(3)	**1.27**			
$\boldsymbol{V_{W(19)}}$ **= 5.56**					
W(24)-O(77)	1.75(3)	**1.57**	W(24)-O(139)	1.99(3)	**0.84**
W(24)-O(20)	1.76(3)	**1.53**	W(24)-O(17)	2.03(3)	**0.74**
W(24)-O(69)	1.78(3)	**1.45**			
$\boldsymbol{V_{W(24)}}$ **= 6.13**					
O(119)-Mn(1)	2.16(2)	**0.37**	Mn(1)-O(1WA)	2.21(3)	**0.32**
Mn(1)-O(119A)	2.16(2)	**0.37**	Mn(1)-O(2WA)	2.31(4)	**0.25**
Mn(1)-O(1W)	2.21(3)	**0.32**	Mn(1)-O(2W)	2.31(4)	**0.25**
$\boldsymbol{V_{Mn(1)}}$ **= 1.88**					
As(1)-O(67)	1.77(3)	**1.05**	As(2)-O(41)	1.65(3)	**1.46**
As(1)-O(47)	1.79(3)	**1.00**	As(2)-O(92)	1.69(3)	**1.31**
As(1)-O(74)	1.81(3)	**0.94**	As(2)-O(122)	1.75(4)	**1.11**
$\boldsymbol{V_{As(1)}}$ **= 2.99**			$\boldsymbol{V_{As(2)}}$ **= 3.88**		
As(3)-O(12)	1.72(3)	**1.21**	As(4)-O(8)	1.76(3)	**1.08**
As(3)-O(2)	1.75(3)	**1.11**	As(4)-O(100)	1.76(3)	**1.08**
As(3)-O(57)	1.78(3)	**1.02**	As(4)-O(93)	1.83(3)	**0.90**
$\boldsymbol{V_{As(3)}}$ **= 3.34**			$\boldsymbol{V_{As(4)}}$ **= 3.06**		

$*V_M = \sum_j S_{M-O_j} = \sum_j \exp(\frac{r_0 - r_{M-O_j}}{0.37})$; r_{Ce-O} =2.220 Å/2.08 Å[a]; r_{W-O} =1.917 Å; r_{As-O} =1.789 Å; r_{Mn-O} =1.790 Å[22]

[a]During the BVS calculation of Ce centers in **3**, the final values are chemically unreasonable based on the standard bond length of Ce^{IV}–O (r_{Ce-O} =2.220 Å). The reasonable values for Ce oxidation states are obtained based on the other standard bond length of r_{Ce-O} =2.080 Å. In fact, we found that the Ce(IV) centers in **3** exhibit a different coordination environment in contrast to those in **1** and **2**, that is, all coordinated O atoms derive from the polyoxoanions, leading to an unusual short Ce–O bond lengths. This coordination mode is quite similar to the reported polyoxoanions $[Ce^{IV}(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{16-}$, $[Ce^{IV}(W_5O_{18})_2]^{8-}$ and $[Ce^{IV}{}_2(PW_{10}O_{38})(PW_{11}O_{39})_2]^{17-}$.[26] In these compounds, the average bond length of Ce(IV)–O is usually in the range of 2.27 ~ 2.36 Å. [26] In **3**, the average bond length of Ce(IV)-O is 2.35 Å.