Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Catalytic Water Oxidation Based on Ag(I)-Substituted Keggin Polyoxotungstophosphate

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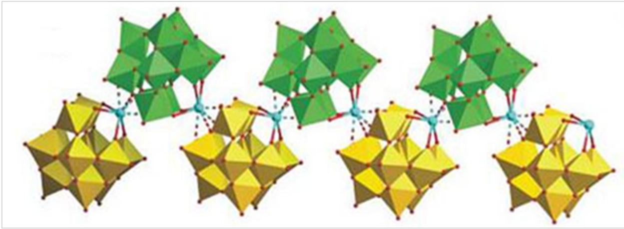

Fig. S1. View of a 1D chain-like structure of $[H_3AgPW_{11}O_{39}]^{3-}$ in the crystal. Polyhedra: $[PW_{11}O_{39}]^{7-}$; blue balls: Ag^{+} [43].

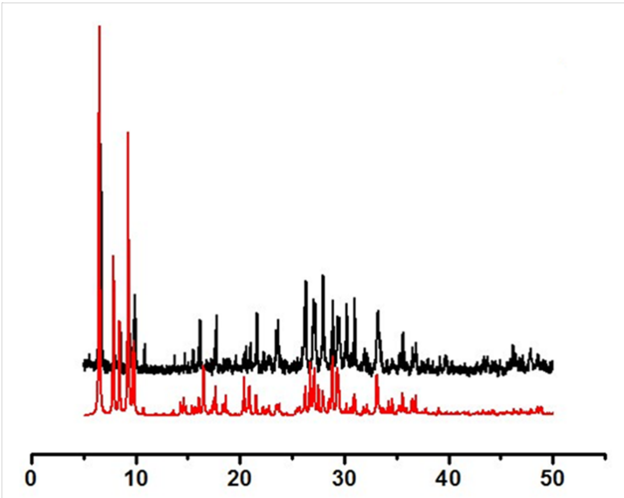

Fig. S2. XRD patterns of $K_3[H_3AgPW_{11}O_{39}]\cdot 12H_2O$ (red: simulated; black: experimental).

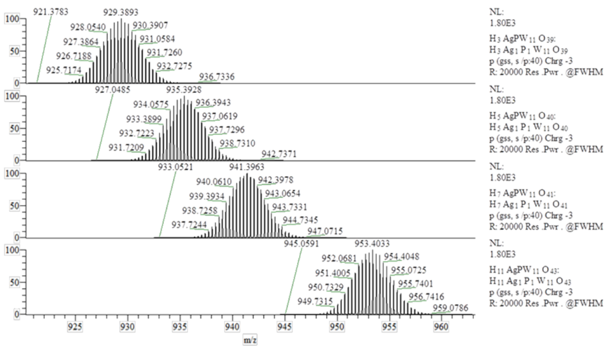

Fig. S3. The simulated isotopic patterns at m/z = 929.7239, 935.3751, 941.3730 and 953.0261 for MS analysis.

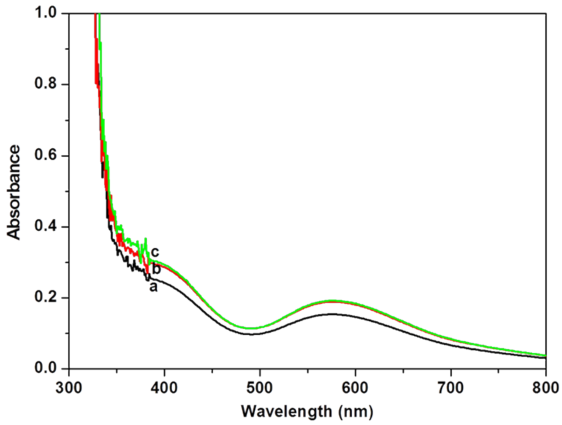

Fig. S4. UV-visible spectra of a solution of $K_3[H_3AgPW_{11}O_{39}]\cdot 12H_2O$ (2 mM) and $Na_2S_2O_8$ (8.8×10^{-2} M) when the solution lasts a: 45 mins; b: 1 h; c: 6 hs.

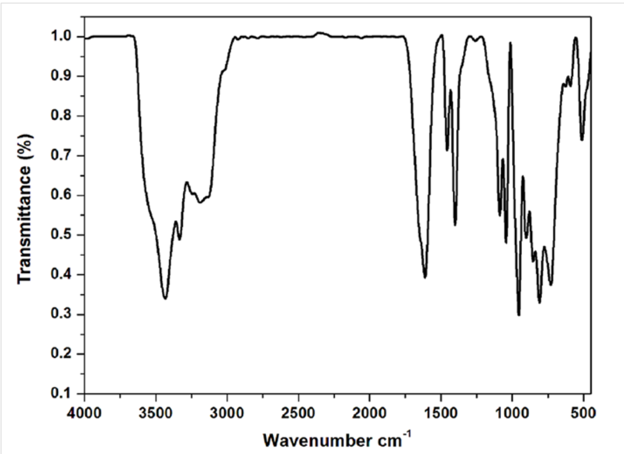

Fig. S5. FT-IR spectrum of $K_3[H_3AgPW_{11}O_{39}]\cdot 12H_2O$.

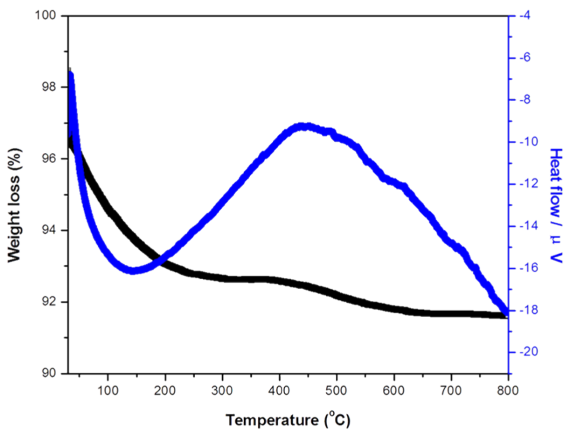

Fig. S6. TG/DTA analysis of $K_3[H_3AgPW_{11}O_{39}]\cdot 12H_2O$.

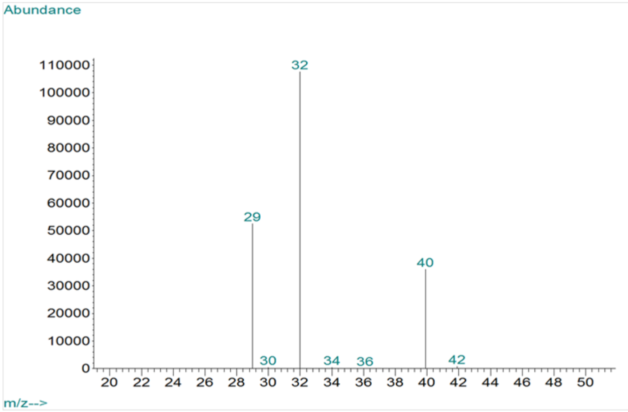

Fig. S7. EI mass spectrum of the gas sample evolved from the catalytic oxidation in 1 M phosphate buffer solution (pH = 5.5) (12 mL) prepared with normal water containing $K_3[H_3Ag^IPW_{11}O_{39}]\cdot 12H_2O$ (2 mM) and $Na_2S_2O_8$ (8.8×10^{-2} M) at 25 °C. The ions with m/z = 28, 32, 34, 36 and 40 were monitored selectively.

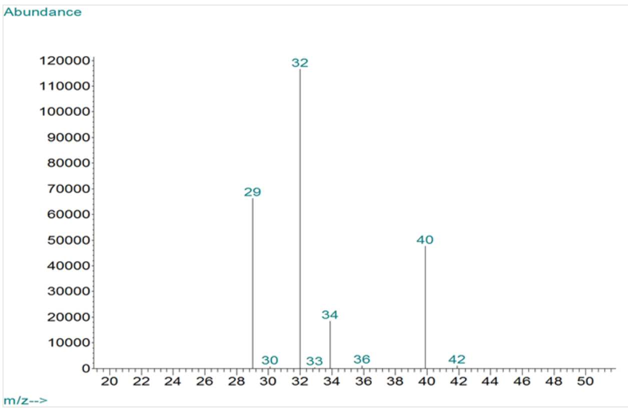

Fig. S8. EI mass spectrum of the gas sample evolved during the catalytic oxidation from the catalytic oxidation in 1 M phosphate buffer solution (pH = 5.5) (12 mL) prepared with $H_2{}^{18}O$-enriched water (8.3% $H_2{}^{18}O$) containing $K_3[H_3Ag^IPW_{11}O_{39}]\cdot 12H_2O$ (2 mM) and $Na_2S_2O_8$ (8.8×10^{-2} M). The ions with m/z = 28, 32, 34, 36 and 40 were monitored selectively.

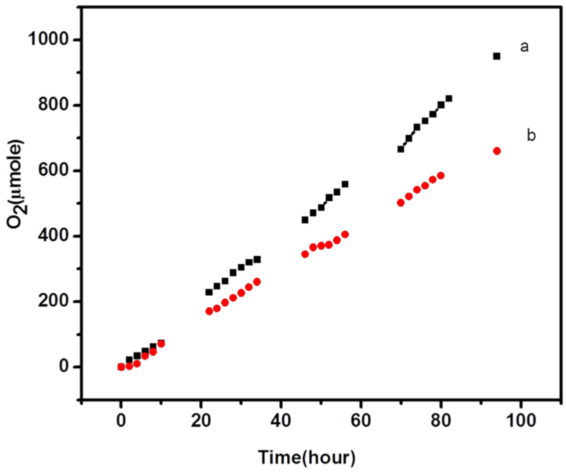

Fig. S9. Time course of O_2 evolution from 200 ml of 17.6×10^{-2} M $Na_2S_2O_8$ solution containing 0.05 mM of a: $K_3[H_3AgPW_{11}O_{39}]\cdot 12H_2O$ b: $AgNO_3$ in 1 M phosphate buffer solution (pH = 5.5) at (24.5±0.5) ^oC.

Table S1. Crystallographic data of $K_3[H_3AgPW_{11}O_{39}]\cdot 12H_2O$

formula	$H_{27}\,Ag\,K_3\,O_{51}\,P\,W_{11}$
formula weight	3121.71
T(K)	296(2)
crystal system, space group	Orthorhombic,Pna2(1)
a,b,c (Å)	17.9123(12), 20.9333(13), 13.3253(9)
α /β /γ (°)	90,90,90
V (Å^3), *Z*	4996.5(6), 4
D_c(mg/m^3)	4.150
F(000)	5472.0
Data / restraints /parameters	11334 / 56 / 613
GOF on F^2	1.104
R_1 [I>2sigma(I)][a]	R_1 = 0.0372,wR_2 =0.1029
wR_2 (all data)[b]	R_1 =0.0498,wR_2 =0.0958

[a] $R_1 = \sum||F_0|-|F_c||/\sum|F_0|$. [b] $wR_2 = [\sum\omega(F_0^2-F_c^2)^2/\sum\omega(F_0^2)^2]^{1/2}$.

Table S2. List of m/z peak assignments in the ESI-MS spectra of $K_3[H_3Ag^IPW_{11}O_{39}]\cdot 12H_2O$ solution

Peak assignments	Observed m/z	Calculated m/z
$[H_3AgPW_{11}O_{39}]^{3-}$	929.7239	929.3893
$[H_3Ag(H_2O)PW_{11}O_{39}]^{3-}$	935.3715	935.3928
$[H_3Ag(H_2O)PW_{11}O_{39}]^{3-}\cdot H_2O$	941.3730	941.3963
$[H_3Ag(H_2O)PW_{11}O_{39}]^{3-}\cdot 2H_2O$	953.0261	953.4033

Table S3. The Ag-O bond lengths of the crystal of $K_3[H_3Ag^IPW_{11}O_{39}]\cdot 12H_2O$ and their bond valence

		Bond length (Å)	S_i	$\sum S_i$	$\sum S_i$
Ag(1)-O(7)	Lacunary O atoms	2.337(15)	0.2355	0.8552	1.2029
Ag(1)-O(19)		2.412(13)	0.2142		
Ag(1)-O(25)		2.425(13)	0.2068		
Ag(1)-O(17)		2.440(14)	0.1987		
Ag(1)-O(1A)	Terminal and bridged O atoms	3.064(15)	0.0347	0.3475	
Ag(1)-O(16A)		2.542(15)	0.1508		
Ag(1)-O(21A)		2.821(15)	0.0709		
Ag(1)-O(35A)		2.737(15)	0.0890		
$Ag-OH_2$		2.268(3)[a]	0.3160		

[b]$S = \exp[(r - r_o)/B]$, where $r_o = 1.842$ and $B = 0.37$

[a] YOU Wan- Sheng，LI Xing- Xing，FANG Yong，CHENG Hong-Wei, Journal of Liaoning Normal University, 2014, 37(2), 221-226.

[b] I. D. Brown and D. Altermatt, Acta Cryst., 1984, B41, 244.

Table S4. Selected bond lengths (Å) and angles (°) for $K_3[H_3AgPW_{11}O_{39}]\cdot12H_2O$

Ag(1)-O(7)	2.377(15)	W(3)-O(3)	1.720(12)
Ag(1)-O(9)	2.412(13)	W(3)-O(9)	1.748(12)
Ag(1)-O(25)	2.425(13)	W(3)-O(33)	1.924(12)
Ag(1)-O(17)	2.440(14)	W(3)-O(20)	1.962(14)
O(7)-K(1)	2.602(13)	W(3)-O(31)	2.116(13)
O(25)-K(1)	2.634(12)	W(3)-O(5)	2.447(11)
K(1)-O(4W)	2.67(2)	W(4)-O(25)	1.769(11)
K(1)-O(19)#2	2.741(13)	W(4)-O(24)	1.935(12)
K(1)-O(8W)	2.83(3)	W(4)-O(16)	1.968(12)
K(1)-O(35)#2	3.071(13)	W(4)-O(21)	2.113(11)
O(19)-K(2)	2.648(13)	W(4)-O(14)	2.347(10)
K(2)-O(11W)	2.72(4)	W(4)-O(25)	1.769(11)
K(2)-O(34)#1	2.724(15)	W(5)-O(26)	1.717(11)
K(2)-O(26)#2	2.788(12)	W(5)-O(21)	1.819(11)
K(2)-O(38)#4	2.878(12)	W(5)-O(2)	1.915(12)
K(2)-O(3W)#1	2.94(2)	W(5)-O(1)	1.940(11)
K(3)-O(6W)	2.73(2)	W(5)-O(18)	1.977(12)
K(3)-O(22)#2	2.859(13)	W(5)-O(12)	2.429(10)
K(3)-O(9W)#4	2.92(3)	W(6)-O(30)	1.735(12)
K(3)-O(28)#4	2.922(12)	W(6)-O(23)	1.869(13)
O(17)-K(3)	2.745(13)	W(6)-O(11)	1.941(12)
O(9)-K(3)	2.862(15)	W(6)-O(8)	1.946(12)
O(22)-K(4)	2.435(13)	W(6)-O(10)	1.950(12)
K(4)-O(10W)	2.243(19)	W(7)-O(28)	1.724(10)
K(4)-O(3)#1	2.376(14)	W(7)-O(31)	1.817(12)
K(4)-O(13)#2	2.420(12)	W(7)-O(8)	1.877(13)
K(4)-O(1W)	2.61(2)	W(7)-O(38)	1.899(12)
K(4)-O(7W)	2.61(3)	W(7)-O(36)	1.938(12)
W(1)-O(13)	1.732(12)	W(8)-O(32)	1.673(13)
W(1)-O(35)	1.828(10)	W(8)-O(15)	1.896(11)
W(1)-O(1)	1.932(10)	W(8)-O(37)	1.898(11)
W(1)-O(37)	1.937(11)	W(8)-O(20)	1.917(14)
W(1)-O(4)	1.983(12)	W(8)-O(38)	1.946(11)
W(1)-O(12)	2.435(10)	W(8)-O(5)	2.398(11)
W(2)-O(17)	1.732(13)	W(9)-O(34)	1.724(13)
W(2)-O(19)	1.739(12)	W(9)-O(7)	1.798(13)
W(2)-O(15)	1.944(10)	W(9)-O(33)	1.895(12)
W(2)-O(16)	1.958(11)	W(9)-O(27)	1.978(14)
W(2)-O(35)	2.125(10)	W(9)-O(23)	2.089(13)
W(2)-O(14)	2.362(10)	W(9)-O(6)	2.473(11)
W(10)-O(39)	1.703(12)	O(17)-W(2)-O(14)	86.5(5)
W(10)-O(27)	1.896(13)	O(19)-W(2)-O(14)	169.4(5)

W(10)-O(24)	1.904(12)	O(15)-W(2)-O(14)	85.0(4)
W(10)-O(2)	1.916(12)	O(16)-W(2)-O(14)	72.9(4)
W(10)-O(11)	1.917(12)	O(35)-W(2)-O(14)	81.6(4)
W(10)-O(6)	2.385(11)	O(3)-W(3)-O(9)	106.9(7)
W(11)-O(29)	1.739(12)	O(3)-W(3)-O(33)	103.8(6)
W(11)-O(10)	1.879(12)	O(9)-W(3)-O(33)	95.4(6)
W(11)-O(36)	1.903(11)	O(3)-W(3)-O(20)	99.9(6)
W(11)-O(18)	1.917(12)	O(9)-W(3)-O(20)	90.8(6)
W(11)-O(4)	1.926(12)	O(33)-W(3)-O(20)	152.6(5)
W(11)-O(12)	2.430(11)	O(3)-W(3)-O(31)	92.9(6)
O(7)-Ag(1)-O(9)	75.2(4)	O(9)-W(3)-O(31)	159.8(6)
O(7)-Ag(1)-O(25)	76.9(5)	O(33)-W(3)-O(31)	83.4(5)
O(9)-Ag(1)-O(25)	123.3(4)	O(20)-W(3)-O(31)	81.7(5)
O(7)-Ag(1)-O(17)	123.7(5)	O(3)-W(3)-O(5)	160.5(5)
O(9)-Ag(1)-O(17)	77.6(5)	O(9)-W(3)-O(5)	90.7(5)
O(25)-Ag(1)-O(17)	78.6(4)	O(33)-W(3)-O(5)	82.4(4)
O(13)-W(1)-O(35)	103.3(6)	O(20)-W(3)-O(5)	70.8(5)
O(13)-W(1)-O(1)	103.4(5)	O(31)-W(3)-O(5)	69.1(4)
O(35)-W(1)-O(1)	91.3(5)	O(22)-W(4)-O(25)	101.5(6)
O(13)-W(1)-O(37)	99.4(5)	O(22)-W(4)-O(24)	102.3(6)
O(35)-W(1)-O(37)	89.3(5)	O(25)-W(4)-O(24)	93.2(6)
O(1)-W(1)-O(37)	156.4(5)	O(22)-W(4)-O(16)	99.2(5)
O(13)-W(1)-O(4)	98.3(6)	O(25)-W(4)-O(16)	96.6(5)
O(35)-W(1)-O(4)	158.3(5)	O(24)-W(4)-O(16)	154.1(5)
O(1)-W(1)-O(4)	85.4(5)	O(22)-W(4)-O(21)	93.8(5)
O(37)-W(1)-O(4)	85.4(5)	O(25)-W(4)-O(21)	164.6(5)
O(13)-W(1)-O(12)	169.7(5)	O(24)-W(4)-O(21)	81.4(5)
O(35)-W(1)-O(12)	86.2(5)	O(16)-W(4)-O(21)	82.9(5)
O(1)-W(1)-O(12)	72.1(4)	O(22)-W(4)-O(14)	170.4(5)
O(37)-W(1)-O(12)	84.4(4)	O(25)-W(4)-O(14)	85.3(5)
O(4)-W(1)-O(12)	72.4(4)	O(24)-W(4)-O(14)	84.0(4)
O(17)-W(2)-O(19)	101.7(6)	O(16)-W(4)-O(14)	73.0(4)
O(17)-W(2)-O(15)	93.7(5)	O(21)-W(4)-O(14)	79.8(4)
O(19)-W(2)-O(15)	100.8(5)	O(26)-W(5)-O(21)	104.8(6)
O(17)-W(2)-O(16)	97.0(5)	O(26)-W(5)-O(2)	102.4(6)
O(19)-W(2)-O(16)	99.3(5)	O(21)-W(5)-O(2)	89.1(5)
O(15)-W(2)-O(16)	154.7(5)	O(26)-W(5)-O(1)	102.8(6)
O(17)-W(2)-O(35)	167.4(6)	O(21)-W(5)-O(1)	90.8(5)
O(19)-W(2)-O(35)	90.6(5)	O(2)-W(5)-O(1)	154.0(5)
O(15)-W(2)-O(35)	81.2(5)	O(26)-W(5)-O(18)	99.8(6)
O(16)-W(2)-O(35)	83.4(5)	O(21)-W(5)-O(18)	155.4(5)
O(2)-W(5)-O(18)	85.2(5)	O(34)-W(9)-O(7)	105.3(8)
O(1)-W(5)-O(18)	84.2(5)	O(34)-W(9)-O(33)	101.9(6)

O(26)-W(5)-O(12)	170.2(5)	O(7)-W(9)-O(33)	94.4(6)
O(21)-W(5)-O(12)	83.9(5)	O(34)-W(9)-O(27)	102.2(7)
O(2)-W(5)-O(12)	82.0(5)	O(7)-W(9)-O(27)	93.0(6)
O(1)-W(5)-O(12)	72.1(4)	O(33)-W(9)-O(27)	151.9(5)
O(18)-W(5)-O(12)	71.7(4)	O(34)-W(9)-O(23)	92.9(7)
O(30)-W(6)-O(23)	102.0(7)	O(7)-W(9)-O(23)	161.7(6)
O(30)-W(6)-O(11)	101.2(6)	O(33)-W(9)-O(23)	83.9(5)
O(23)-W(6)-O(11)	88.4(6)	O(27)-W(9)-O(23)	80.6(6)
O(30)-W(6)-O(8)	102.2(6)	O(34)-W(9)-O(6)	163.2(7)
O(23)-W(6)-O(8)	91.9(6)	O(7)-W(9)-O(6)	90.3(5)
O(11)-W(6)-O(8)	156.0(5)	O(33)-W(9)-O(6)	82.6(4)
O(30)-W(6)-O(10)	104.4(7)	O(27)-W(9)-O(6)	70.2(4)
O(23)-W(6)-O(10)	153.5(5)	O(23)-W(9)-O(6)	71.4(4)
O(11)-W(6)-O(10)	84.9(5)	O(39)-W(10)-O(27)	101.2(6)
O(8)-W(6)-O(10)	84.2(5)	O(39)-W(10)-O(24)	103.8(6)
O(28)-W(7)-O(31)	103.0(6)	O(27)-W(10)-O(24)	90.6(6)
O(28)-W(7)-O(8)	102.3(6)	O(39)-W(10)-O(2)	100.9(6)
O(31)-W(7)-O(8)	90.2(6)	O(27)-W(10)-O(2)	157.6(5)
O(28)-W(7)-O(38)	101.1(5)	O(24)-W(10)-O(2)	87.7(5)
O(31)-W(7)-O(38)	90.0(6)	O(39)-W(10)-O(11)	99.3(6)
O(8)-W(7)-O(38)	156.0(5)	O(27)-W(10)-O(11)	87.2(6)
O(28)-W(7)-O(36)	102.9(5)	O(24)-W(10)-O(11)	156.8(5)
O(31)-W(7)-O(36)	154.0(5)	O(2)-W(10)-O(11)	85.7(5)
O(8)-W(7)-O(36)	83.7(5)	O(39)-W(10)-O(6)	172.7(5)
O(38)-W(7)-O(36)	85.7(5)	O(27)-W(10)-O(6)	73.5(5)
O(32)-W(8)-O(15)	103.3(6)	O(24)-W(10)-O(6)	81.6(4)
O(32)-W(8)-O(37)	101.5(5)	O(2)-W(10)-O(6)	84.1(5)
O(15)-W(8)-O(37)	87.7(5)	O(11)-W(10)-O(6)	75.7(5)
O(32)-W(8)-O(20)	100.0(6)	O(29)-W(11)-O(10)	102.2(6)
O(15)-W(8)-O(20)	90.3(5)	O(29)-W(11)-O(36)	101.3(6)
O(37)-W(8)-O(20)	158.3(5)	O(10)-W(11)-O(36)	85.4(5)
O(32)-W(8)-O(38)	100.6(6)	O(29)-W(11)-O(18)	101.4(6)
O(15)-W(8)-O(38)	155.9(5)	O(10)-W(11)-O(18)	88.6(5)
O(37)-W(8)-O(38)	85.0(5)	O(36)-W(11)-O(18)	157.3(5)
O(20)-W(8)-O(38)	88.1(5)	O(29)-W(11)-O(4)	101.4(6)
O(32)-W(8)-O(5)	170.6(5)	O(10)-W(11)-O(4)	156.2(5)
O(15)-W(8)-O(5)	82.8(4)	O(36)-W(11)-O(4)	88.1(5)
O(37)-W(8)-O(5)	85.7(4)	O(18)-W(11)-O(4)	88.7(5)
O(20)-W(8)-O(5)	72.6(5)	O(29)-W(11)-O(12)	171.9(6)
O(38)-W(8)-O(5)	73.8(4)	O(10)-W(11)-O(12)	83.3(5)
O(18)-W(11)-O(12)	72.6(4)	O(36)-W(11)-O(12)	84.9(4)
O(4)-W(11)-O(12)	73.4(4)		

#1 -x+1, -y+1, z-1/2; #2 -x+1, -y+1, z+1/2; #3 x+1/2, -y+3/2, z; #4 x-1/2, -y+3/2, z