

Transformation of Tri-Titanium(IV)-Substituted α -Keggin Polyoxometalate (POM) into Tetra-Titanium(IV)-Substituted POMs: Reaction Products of Titanium(IV) Sulfate with the Dimeric Keggin POM Precursor under Acidic Conditions

Yuki Mouri, Yoshitaka Sakai, Yoshitaka Kobayashi, Shoko Yoshida and Kenji Nomiya *

Figure S1. ^{183}W -NMR spectra of (a) $\text{K}_3[\{\text{Ti}_4(\mu\text{-O})_3(\text{SO}_4)_2(\text{H}_2\text{O})_8\}(\alpha\text{-PW}_9\text{O}_{34})]\cdot 6\text{H}_2\text{O}$ (K-2) in 0.5 M aqueous H_2SO_4 , and (b) $\text{K}_{10}\text{H}_2[(\alpha\text{-1,2,3-PW}_9\text{Ti}_3\text{O}_{37})_2\text{O}_3]\cdot 15\text{H}_2\text{O}$ as a precursor in D_2O .

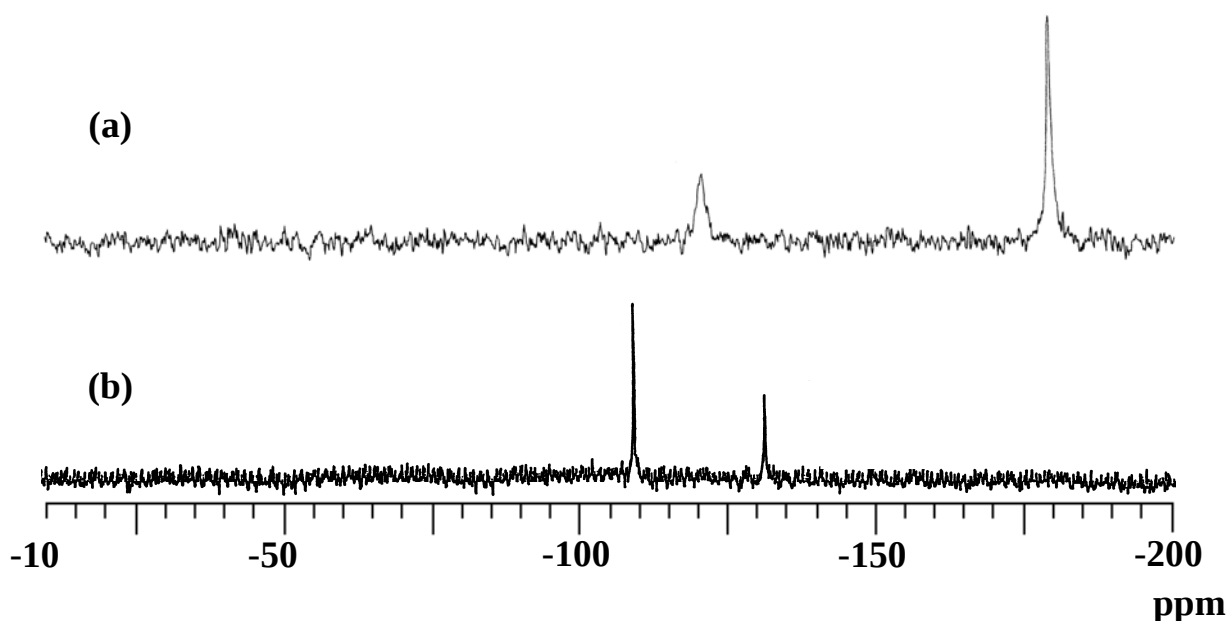


Table S1. Bond lengths ($\text{\AA}$) and angles ($^\circ$) for **1**.

W-O_t (O_t: terminal oxygen)	
W(1)-O(1)	1.710(10)
W(2)-O(2)	1.715(11)
W(3)-O(3)	1.719(11)
W(4)-O(13)	1.717(9)
W(5)-O(14)	1.709(10)
W(6)-O(15)	1.713(11)
W(7)-O(16)	1.719(9)
W(8)-O(17)	1.706(11)
W(9)-O(18)	1.708(10)
average = 1.713 [1.706(11)-1.719(10)]	

Table S1. Cont.

W-O_c (O_c: corner-sharing oxygen)	
W(1)-O(7)	1.856(9)
W(1)-O(12)	1.903(10)
W(2)-O(8)	1.889(10)
W(2)-O(9)	1.861(10)
W(3)-O(10)	1.910(10)
W(3)-O(11)	1.862(11)
W(4)-O(24)	1.894(9)
W(4)-O(7)	1.965(9)
W(5)-O(20)	1.915(9)
W(5)-O(8)	1.972(9)
W(6)-O(20)	1.905(9)
W(6)-O(9)	1.976(10)
W(7)-O(22)	1.930(10)
W(7)-O(10)	1.942(10)
W(8)-O(22)	1.877(10)
W(8)-O(11)	1.984(10)
W(9)-O(24)	1.923(9)
W(9)-O(12)	1.927(9)
average = 1.916 [1.856(9)-1.984(10)]	
W-O_c (O_c: corner-sharing oxygen coordinating to Ti atom)	
W(7)-O(28)	1.848(9)
W(6)-O(27)	1.832(9)
average = 1.840 [1.832(9)-1.848(9)]	
W-O_e (O_e: edge-sharing oxygen)	
W(1)-O(4)	1.902(10)
W(1)-O(6)	1.941(10)
W(2)-O(5)	1.909(11)
W(2)-O(4)	1.949(10)
W(3)-O(6)	1.915(10)
W(3)-O(5)	1.955(11)
W(4)-O(19)	1.944(9)
W(5)-O(19)	1.926(9)
W(6)-O(21)	1.926(10)
W(7)-O(21)	1.914(11)
W(8)-O(23)	1.952(10)
W(9)-O(23)	1.897(9)
average = 1.928 [1.897(9)-1.955(11)]	

Table S1. *Cont.*

W-O_e (O_e: edge-sharing oxygen coordinating to Ti atom)		
W(4)-O(25)	1.839(8)	
W(5)-O(26)	1.828(9)	
W(8)-O(29)	1.817(9)	
W(9)-O(30)	1.866(9)	
		average = 1.838 [1.817(9)-1.866(9)]
W-O_a (oxygen coordinating to P atom)		
W(1)-O(37)	2.423(9)	
W(2)-O(37)	2.423(10)	
W(3)-O(37)	2.411(9)	
W(4)-O(34)	2.498(9)	
W(5)-O(34)	2.380(9)	
W(6)-O(35)	2.377(10)	
W(7)-O(35)	2.355(9)	
W(8)-O(36)	2.455(8)	
W(9)-O(36)	2.489(9)	
		average = 2.423 [2.355(9)-2.498(9)]
P-O		
P(1)-O(34)	1.545(9)	
P(1)-O(35)	1.518(9)	
P(1)-O(36)	1.544(9)	
P(1)-O(37)	1.557(9)	
		average = 1.541 [1.518(9)-1.557(9)]
O-P-O		
O(34)-P(1)-O(35)	110.7(5)	
O(34)-P(1)-O(36)	109.7(5)	
O(34)-P(1)-O(37)	108.4(5)	
O(35)-P(1)-O(36)	110.4(5)	
O(35)-P(1)-O(37)	109.4(5)	
O(36)-P(1)-O(37)	108.1(5)	
		average = 109.5 [108.1(5)-110.7(5)]

Table S2. Bond lengths (Å) and angles (°) for **2**

W-O_t (O_t: terminal oxygen)	
W(1)-O(1)	1.716(6)
W(2)-O(2)	1.717(6)
W(3)-O(3)	1.706(6)
W(4)-O(13)	1.708(6)
W(5)-O(14)	1.719(6)
W(6)-O(15)	1.719(6)
W(7)-O(16)	1.729(5)
W(8)-O(17)	1.713(6)
W(9)-O(18)	1.719(6)
average = 1.716 [1.706(6)-1.729(5)]	
W-O_c (O_c: corner-sharing oxygen)	
W(1)-O(7)	1.877(6)
W(1)-O(12)	1.875(6)
W(2)-O(8)	1.932(6)
W(2)-O(9)	1.856(6)
W(3)-O(10)	1.884(5)
W(3)-O(11)	1.845(6)
W(4)-O(24)	1.879(6)
W(4)-O(7)	1.960(6)
W(5)-O(20)	1.943(5)
W(5)-O(8)	1.884(6)
W(6)-O(20)	1.872(5)
W(6)-O(9)	1.995(6)
W(7)-O(22)	1.947(5)
W(7)-O(10)	1.933(5)
W(8)-O(22)	1.877(5)
W(8)-O(11)	1.984(6)
W(9)-O(24)	1.920(6)
W(9)-O(12)	1.966(6)
average = 1.913 [1.845(6)-1.995(6)]	
W-O_c (O_c: corner-sharing oxygen coordinating to Ti atoms)	
W(4)-O(25)	1.862(6)
W(5)-O(26)	1.932(6)
W(6)-O(27)	1.843(5)
W(7)-O(28)	1.856(5)
W(8)-O(29)	1.855(6)
W(9)-O(30)	1.862(6)
average = 1.868 [1.843(5)-1.932(6)]	

Table S2. *Cont.*

W-O_e (O_e: edge-sharing oxygen)			
W(1)-O(4)	1.930(6)	W(8)-O(23)	1.926(6)
W(1)-O(6)	1.942(6)	W(9)-O(23)	1.908(6)
W(2)-O(5)	1.907(6)		
W(2)-O(4)	1.961(6)		
W(3)-O(6)	1.943(6)		
W(3)-O(5)	1.966(6)		
W(4)-O(19)	1.934(6)		
W(5)-O(19)	1.903(6)		
W(6)-O(21)	1.946(5)		
W(7)-O(21)	1.884(5)		
average = 1.929 [1.884(5)-1.966(6)]			
W-O_a (oxygen coordinating to P atom)			
W(1)-O(34)	2.354(5)		
W(2)-O(34)	2.380(5)		
W(3)-O(34)	2.364(5)		
W(4)-O(31)	2.394(5)		
W(5)-O(31)	2.308(5)		
W(6)-O(32)	2.378(5)		
W(7)-O(32)	2.332(5)		
W(8)-O(33)	2.377(5)		
W(9)-O(33)	2.340(5)		
average = 2.359 [2.308(5)-2.394(5)]			
P-O			
P(1)-O(31)	1.535(5)		
P(1)-O(32)	1.521(5)		
P(1)-O(33)	1.528(5)		
P(1)-O(34)	1.582(5)		
average = 1.542 [1.521(5)-1.582(5)]			
S-O			
S(1)-O(1X)	1.489(6)	S(2)-O(5X)	1.505(5)
S(1)-O(2X)	1.470(6)	S(2)-O(6X)	1.489(6)
S(1)-O(3X)	1.500(6)	S(2)-O(7X)	1.474(6)
S(1)-O(4X)	1.455(6)	S(2)-O(8X)	1.456(6)
average = 1.480 [1.455(6)-1.505(5)]			
O-P-O			
O(31)-P(1)-O(32)	112.2(3)		
O(31)-P(1)-O(33)	112.2(3)		
O(31)-P(1)-O(34)	106.9(3)		
O(32)-P(1)-O(33)	111.9(3)		
O(32)-P(1)-O(34)	106.6(3)		
O(33)-P(1)-O(34)	106.7(3)		
average = 109.4 [106.6(3)-112.2(3)]			

Table S2. *Cont.*

O-S-O			
O(1X)-S(1)-O(2X)	109.3(4)	O(4X)-S(1)-O(5X)	110.2(3)
O(1X)-S(1)-O(3X)	109.7(3)	O(4X)-S(1)-O(6X)	107.7(3)
O(1X)-S(1)-O(7X)	108.7(4)	O(4X)-S(1)-O(8X)	107.9(3)
O(2X)-S(1)-O(3X)	109.5(4)	O(5X)-S(1)-O(6X)	109.5(3)
O(2X)-S(1)-O(7X)	111.0(4)	O(5X)-S(1)-O(8X)	110.4(3)
O(3X)-S(1)-O(7X)	108.7(4)	O(6X)-S(1)-O(8X)	111.1(4)
average = 109.5 [107.7(3)-111.1(4)]			

Table S3. Bond valence sum (BVS) calculations of W, Ti, O and P atoms for **K-1**.

O(1)	1.750	O(32)	1.951	W(1)	6.201
O(2)	1.726	O(33)	1.965	W(2)	6.162
O(3)	1.708	O(34)	1.925	W(3)	6.057
O(4)	1.958	O(35)	1.901	W(4)	6.032
O(5)	1.924	O(36)	1.939	W(5)	6.155
O(6)	1.942	O(37)	1.949	W(6)	6.144
O(7)	2.057	O(38)	1.980	W(7)	6.127
O(8)	1.941			W(8)	6.171
O(9)	2.016	O(1W)	0.489	W(9)	6.133
O(10)	1.954	O(2W)	0.374		
O(11)	1.994	O(3W)	0.462	Ti(1)	4.178
O(12)	2.012	O(4W)	0.440	Ti(2)	4.202
O(13)	1.717	O(5W)	0.391	Ti(3)	4.088
O(14)	1.754	O(6W)	0.467	Ti(4)	4.236
O(15)	1.736				
O(16)	1.708			P(1)	4.916
O(17)	1.769				
O(18)	1.759				
O(19)	1.906				
O(20)	2.038				
O(21)	1.984				
O(22)	2.079				
O(23)	1.966				
O(24)	2.048				
O(25)	1.819				
O(26)	1.877				
O(27)	2.038				
O(28)	2.065				
O(29)	1.836				
O(30)	1.799				
O(31)	2.012				

Table S4. Bond valence sum (BVS) calculations of W, Ti, S, O and P atoms for **K-2**.

O(1)	1.722	O(32)	1.910	W(1)	6.163
O(2)	1.717	O(33)	1.879	W(2)	6.057
O(3)	1.769	O(34)	1.991	W(3)	6.184
O(4)	1.853			W(4)	6.147
O(5)	1.903	O(1M)	2.046	W(5)	6.080
O(6)	1.867	O(2M)	2.089	W(6)	6.111
O(7)	2.004	O(3M)	2.080	W(7)	6.140
O(8)	2.053			W(8)	6.130
O(9)	1.989	O(1W)	0.400	W(9)	6.080
O(10)	2.051	O(2W)	0.463		
O(11)	2.049	O(3W)	0.467	Ti(1)	4.210
O(12)	1.996	O(4W)	0.417	Ti(2)	4.238
O(13)	1.759	O(5W)	0.421	Ti(3)	4.177
O(14)	1.708	O(6W)	0.434	Ti(4)	4.257
O(15)	1.708	O(7W)	0.387		
O(16)	1.662	O(8W)	0.478	P(1)	4.915
O(17)	1.736				
O(18)	1.708	O(1X)	1.943	S(1)	5.933
O(19)	1.994	O(2X)	1.516	S(2)	5.894
O(20)	2.061	O(3X)	1.884		
O(21)	2.018	O(4X)	1.905		
O(22)	2.036	O(5X)	1.900		
O(23)	2.001	O(6X)	1.500		
O(24)	2.100	O(7X)	1.579		
O(25)	2.020	O(8X)	1.575		
O(26)	1.965				
O(27)	2.050				
O(28)	2.000				
O(29)	2.037				
O(30)	2.045				
O(31)	1.871				