

Novel Ti-O-Ti Bonding Species Constructed in a Metal-Oxide Cluster. Reaction Products of Bis(oxalato)oxotitanate(IV) with the Dimeric, 1,2-Di-Titanium(IV)-Substituted Keggin Polyoxotungstate

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Fig. S1 Temperature-dependent ^{31}P NMR of **1** in D_2O : (a) at 23.2 °C, (b) at 49.7 °C, (c) at 79.7 °C, and (d) the solution of (c) remeasured at 23.0 °C.

Table S1 Average bond distances (\AA) and angles (°) [range] for the Keggin POM moiety in **1a**

Table S2 Bond valence sum (BVS) calculations of W(1-10), Ti(1-4), P and O atoms

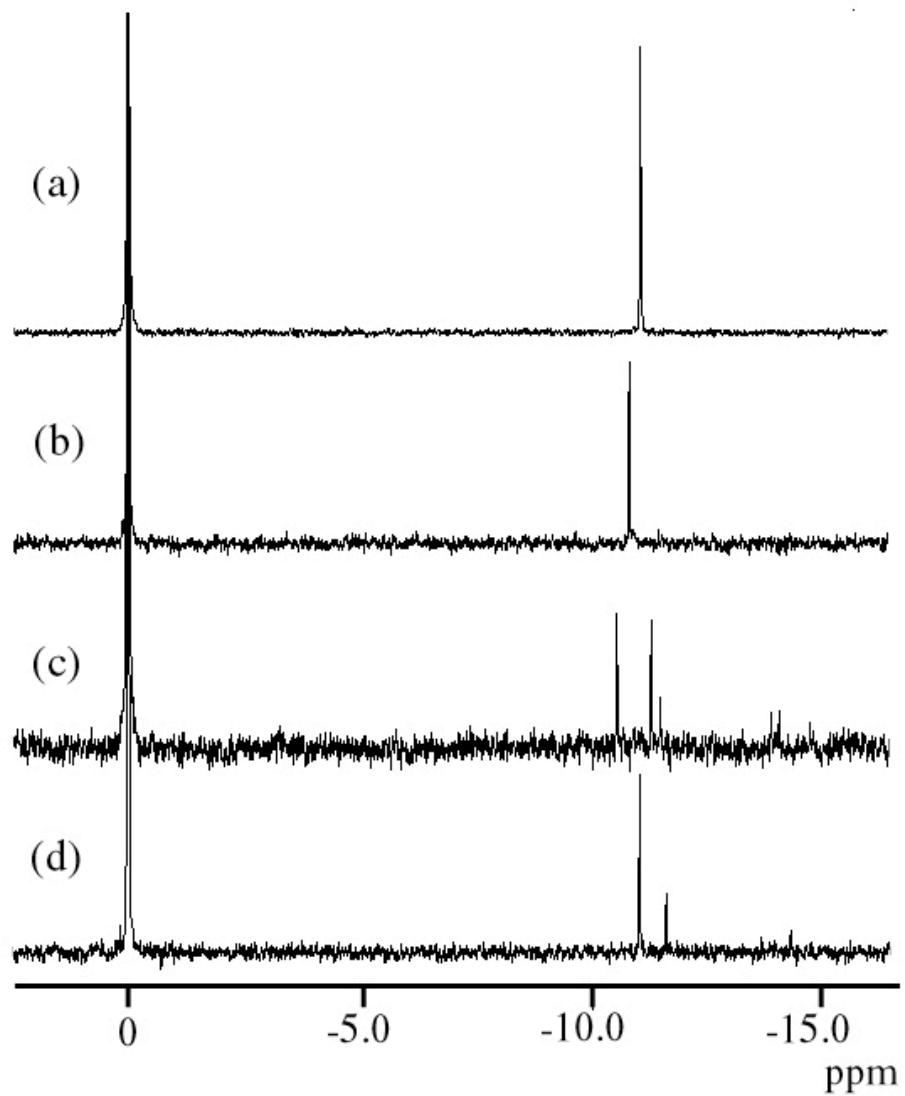


Fig. S1

Table S1 Average bond distances (\AA) and angles ($^\circ$) [range] for the Keggin POM moiety in **1a**

W-Ot (Ot : terminal oxygen)	1.710 [1.682(12) – 1.723(10)]
W-Oc (Oc : corner sharing oxygen)	1.907 [1.862(10) – 1.969(10)]
W-Oe (Oe : edge-sharing oxygen)	1.921 [1.872(10) – 1.979(11)]
W-Oa (Oa : oxygen coordinated to P atom)	2.407 [2.335(10) – 2.473(10)]
W-Ob (Ob : oxygen coordinated to Ti atom)	1.870 [1.854(11) – 1.897(10)]
P-O distance	1.539 [1.517(10) - 1.559(10)]
O-P-O angles	109.5 [106.8(5) – 111.6(6)]

Table S2 Bond valence sum(BVS) calcutions of W(1-10), Ti(1-4), P and O atoms

W(1)	6.174	W(6)	6.104
W(2)	6.288	W(7)	6.205
W(3)	6.148	W(8)	6.189
W(4)	6.299	W(9)	6.083
W(5)	6.180	W(10)	6.161
W(1-10) average = 6.183 [6.083-6.299]			
Ti(1)	4.294	Ti(3)	4.278
Ti(2)	4.182	Ti(4)	4.252
Ti(1-4) average = 4.252 [4.182-4.294]			
P(1)	4.947		
O(1)	2.145	O(16)	1.726
O(2)	1.731	O(17)	2.023
O(3)	2.113	O(18)	1.731
O(4)	1.984	O(19)	2.089
O(5)	2.051	O(20)	1.812
O(6)	2.104	O(21)	2.032
O(7)	2.101	O(22)	1.873
O(8)	2.059	O(23)	1.884
O(9)	1.925	O(24)	1.907
O(10)	1.887	O(25)	1.963
O(11)	2.104	O(26)	2.131
O(12)	1.717	O(27)	1.956
O(13)	2.030	O(28)	1.949
O(14)	1.783	O(29)	2.034
O(15)	2.116	O(30)	1.971
