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Synthesis and structure of dinuclear hafnium(IV) and zirconum(IV) complexes sandwiched between 2 mono-lacunary α-Keggin polyoxometalates†

Kenji Nomiya, Yoshio Saku, Shingo Yamada, Wataru Takahashi, Hiromi Sekiya, Akira Shinohara, Megumi Ishimaru and Yoshitaka Sakai

Department of Materials Science, Faculty of Science, Kanagawa University, Hiratsuka, Kanagawa 259-1293, Japan

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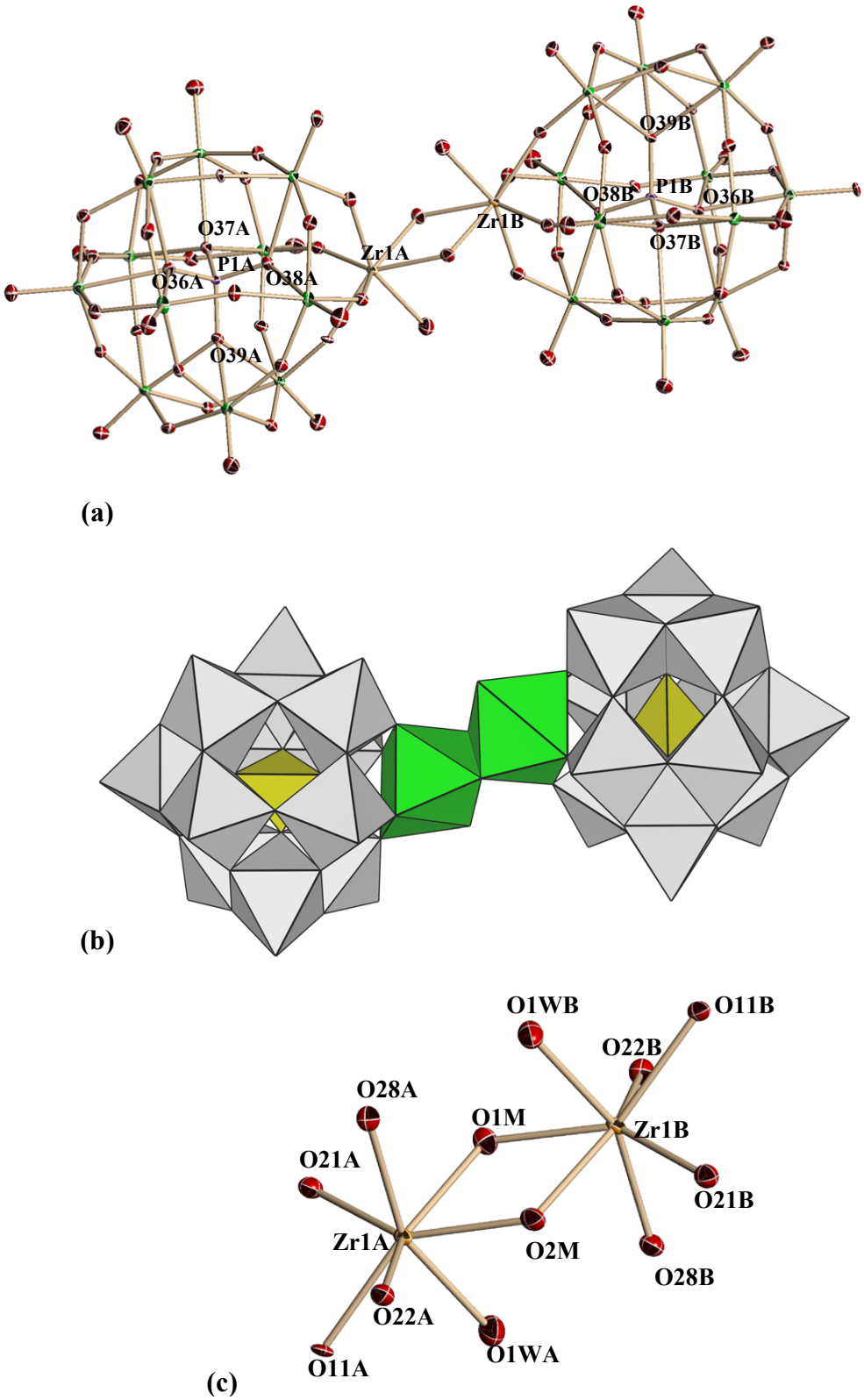

Fig. S1

Table S1 Bond lengths (Å) and angles (°) for **1**

W-O_t (O_t : terminal oxygen)			
W(1A)-O(1A)	1.720(15)	W(1B)-O(1B)	1.682(14)
W(2A)-O(2A)	1.716(14)	W(2B)-O(2B)	1.718(13)
W(3A)-O(3A)	1.705(13)	W(3B)-O(3B)	1.708(13)
W(4A)-O(13A)	1.722(14)	W(4B)-O(13B)	1.705(13)
W(5A)-O(14A)	1.742(14)	W(5B)-O(14B)	1.745(14)
W(6A)-O(15A)	1.691(13)	W(6B)-O(15B)	1.701(13)
W(7A)-O(16A)	1.699(15)	W(7B)-O(16B)	1.735(14)
W(8A)-O(17A)	1.717(14)	W(8B)-O(17B)	1.695(13)
W(9A)-O(30A)	1.706(14)	W(9B)-O(30B)	1.715(14)
W(10A)-O(31A)	1.699(14)	W(10B)-O(31B)	1.691(15)
W(11A)-O(32A)	1.699(13)	W(11B)-O(32B)	1.720(14)
		average = 1.711 [1.682(14)-1.745(14)]	
W-O_c (O_c : corner-sharing oxygen)			
W(1A)-O(7A)	1.903(14)	W(1B)-O(7B)	1.869(12)
W(1A)-O(12A)	1.883(13)	W(1B)-O(12B)	1.874(13)
W(2A)-O(8A)	1.985(13)	W(2B)-O(8B)	1.967(12)
W(2A)-O(9A)	1.891(12)	W(2B)-O(9B)	1.911(12)
W(3A)-O(10A)	1.910(13)	W(3B)-O(10B)	1.929(12)
W(3A)-O(11A)	1.802(13)	W(3B)-O(11B)	1.805(12)
W(4A)-O(23A)	1.843(13)	W(4B)-O(23B)	1.876(13)
W(4A)-O(7A)	1.919(13)	W(4B)-O(7B)	1.942(12)
W(5A)-O(19A)	1.917(13)	W(5B)-O(19B)	1.906(13)
W(5A)-O(8A)	1.862(13)	W(5B)-O(8B)	1.873(12)
W(6A)-O(19A)	1.899(13)	W(6B)-O(19B)	1.919(13)
W(6A)-O(9A)	1.922(13)	W(6B)-O(9B)	1.910(12)
W(7A)-O(21A)	1.800(12)	W(7B)-O(21B)	1.801(12)
W(7A)-O(10A)	1.930(13)	W(7B)-O(10B)	1.927(12)
W(8A)-O(22A)	1.807(14)	W(8B)-O(22B)	1.813(14)
W(8A)-O(23A)	2.018(13)	W(8B)-O(23B)	1.985(13)
W(8A)-O(12A)	1.928(13)	W(8B)-O(12B)	1.934(13)
W(9A)-O(33A)	1.856(13)	W(9B)-O(33B)	1.886(13)
W(9A)-O(34A)	1.926(12)	W(9B)-O(34B)	1.939(14)
W(10A)-O(34A)	1.883(13)	W(10B)-O(34B)	1.880(14)

Table S1 continued

W(10A)-O(35A)	1.881(12)	W(10B)-O(35B)	1.856(13)
W(11A)-O(35A)	1.959(11)	W(11B)-O(35B)	1.962(12)
W(11A)-O(33A)	1.986(13)	W(11B)-O(33B)	1.950(13)
W(11A)-O(28A)	1.837(13)	W(11B)-O(28B)	1.821(14)
		average = 1.898 [1.800(12)-2.018(13)]	
W-O_e (O_e : edge-sharing oxygen)			
W(1A)-O(4A)	1.933(13)	W(1B)-O(4B)	1.926(13)
W(1A)-O(6A)	1.942(14)	W(1B)-O(6B)	1.949(13)
W(2A)-O(5A)	1.852(13)	W(2B)-O(5B)	1.854(13)
W(2A)-O(4A)	1.944(13)	W(2B)-O(4B)	1.906(12)
W(3A)-O(6A)	1.926(13)	W(3B)-O(6B)	1.929(13)
W(3A)-O(5A)	1.999(13)	W(3B)-O(5B)	1.999(13)
W(4A)-O(24A)	1.918(14)	W(4B)-O(24B)	1.890(14)
W(4A)-O(18A)	1.978(13)	W(4B)-O(18B)	1.947(12)
W(5A)-O(25A)	1.994(12)	W(5B)-O(25B)	1.970(12)
W(5A)-O(18A)	1.905(12)	W(5B)-O(18B)	1.910(11)
W(6A)-O(26A)	1.911(12)	W(6B)-O(26B)	1.918(14)
W(6A)-O(20A)	1.858(13)	W(6B)-O(20B)	1.872(14)
W(7A)-O(27A)	1.949(12)	W(7B)-O(27B)	1.944(13)
W(7A)-O(20A)	1.968(13)	W(7B)-O(20B)	1.966(13)
W(8A)-O(29A)	1.919(13)	W(8B)-O(29B)	1.916(13)
W(9A)-O(25A)	1.932(13)	W(9B)-O(25B)	1.932(13)
W(9A)-O(24A)	1.915(13)	W(9B)-O(24B)	1.957(14)
W(10A)-O(26A)	1.981(12)	W(10B)-O(26B)	1.921(14)
W(10A)-O(27A)	1.912(12)	W(10B)-O(27B)	1.944(13)
W(11A)-O(29A)	1.933(13)	W(11B)-O(29B)	1.911(13)
		average = 1.931 [1.854(12)-1.999(13)]	
W-O_a (oxygen coordinating to P atom)			
W(1A)-O(39A)	2.415(13)	W(1B)-O(39B)	2.424(12)
W(2A)-O(39A)	2.517(14)	W(2B)-O(39B)	2.474(12)
W(3A)-O(39A)	2.397(14)	W(3B)-O(39B)	2.429(12)
W(4A)-O(36A)	2.425(11)	W(4B)-O(36B)	2.461(11)
W(5A)-O(36A)	2.386(12)	W(5B)-O(36B)	2.357(12)
W(6A)-O(37A)	2.467(12)	W(6B)-O(37B)	2.471(12)
W(7A)-O(37A)	2.434(12)	W(7B)-O(37B)	2.437(12)

Table S1 continued

W(8A)-O(38A)	2.353(11)	W(8B)-O(38B)	2.378(11)
W(9A)-O(36A)	2.471(12)	W(9B)-O(36B)	2.463(12)
W(10A)-O(37A)	2.408(12)	W(10B)-O(37B)	2.396(12)
W(11A)-O(38A)	2.379(12)	W(11B)-O(38B)	2.390(12)
		average = 2.424 [2.353(11)-2.517(14)]	
P-O			
P(1A)-O(36A)	1.533(13)	P(1B)-O(36B)	1.550(13)
P(1A)-O(37A)	1.551(12)	P(1B)-O(37B)	1.545(12)
P(1A)-O(38A)	1.523(13)	P(1B)-O(38B)	1.495(13)
P(1A)-O(39A)	1.536(14)	P(1B)-O(39B)	1.541(13)
		average = 1.534 [1.495(13)-1.551(12)]	
O-P-O			
		O(38B)-P(1B)-O(36B)	
O(38A)-P(1A)-O(36A)	109.4(7)	)	111.0(7)
		O(38B)-P(1B)-O(39B)	
O(38A)-P(1A)-O(39A)	109.8(7)	)	110.8(7)
		O(36B)-P(1B)-O(39B)	
O(36A)-P(1A)-O(39A)	108.5(7)	)	107.5(7)
		O(38B)-P(1B)-O(37B)	
O(38A)-P(1A)-O(37A)	109.9(7)	)	110.5(7)
		O(36B)-P(1B)-O(37B)	
O(36A)-P(1A)-O(37A)	109.3(7)	)	107.4(7)
		O(39B)-P(1B)-O(37B)	
O(39A)-P(1A)-O(37A)	109.9(7)	)	109.6(7)
		average = 109.5 [107.4(7)-111.0(7)]	

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

W-O_t (O_t : terminal oxygen)			
W(1A)-O(1A)	1.698(10)	W(1B)-O(1B)	1.705(10)
W(2A)-O(2A)	1.688(11)	W(2B)-O(2B)	1.704(10)
W(3A)-O(3A)	1.707(11)	W(3B)-O(3B)	1.704(10)
W(4A)-O(13A)	1.698(10)	W(4B)-O(13B)	1.709(10)
W(5A)-O(14A)	1.719(11)	W(5B)-O(14B)	1.713(10)
W(6A)-O(15A)	1.705(11)	W(6B)-O(15B)	1.681(11)
W(7A)-O(16A)	1.703(11)	W(7B)-O(16B)	1.720(10)
W(8A)-O(17A)	1.716(11)	W(8B)-O(17B)	1.707(11)
W(9A)-O(30A)	1.705(11)	W(9B)-O(30B)	1.707(10)
W(10A)-O(31A)	1.725(11)	W(10B)-O(31B)	1.711(10)
W(11A)-O(32A)	1.706(10)	W(11B)-O(32B)	1.718(10)
		average = 1.706 [1.681(11)-1.725(11)]	
W-O_c (O_c : corner-sharing oxygen)			
W(1A)-O(7A)	1.890(10)	W(1B)-O(7B)	1.868(10)
W(1A)-O(12A)	1.889(10)	W(1B)-O(12B)	1.880(10)
W(2A)-O(8A)	1.968(10)	W(2B)-O(8B)	1.947(10)
W(2A)-O(9A)	1.879(9)	W(2B)-O(9B)	1.927(10)
W(3A)-O(10A)	1.907(10)	W(3B)-O(10B)	1.938(10)
W(3A)-O(11A)	1.799(10)	W(3B)-O(11B)	1.792(10)
W(4A)-O(23A)	1.836(10)	W(4B)-O(23B)	1.849(10)
W(4A)-O(7A)	1.925(10)	W(4B)-O(7B)	1.944(9)
W(5A)-O(19A)	1.919(10)	W(5B)-O(19B)	1.910(10)
W(5A)-O(8A)	1.860(10)	W(5B)-O(8B)	1.883(9)
W(6A)-O(19A)	1.913(10)	W(6B)-O(19B)	1.922(10)
W(6A)-O(9A)	1.920(9)	W(6B)-O(9B)	1.897(9)
W(7A)-O(21A)	1.803(10)	W(7B)-O(21B)	1.792(10)
W(7A)-O(10A)	1.936(9)	W(7B)-O(10B)	1.918(9)
W(8A)-O(22A)	1.807(10)	W(8B)-O(22B)	1.814(10)
W(8A)-O(23A)	1.998(11)	W(8B)-O(23B)	2.001(10)
W(8A)-O(12A)	1.924(10)	W(8B)-O(12B)	1.930(10)
W(9A)-O(33A)	1.846(10)	W(9B)-O(33B)	1.878(10)
W(9A)-O(34A)	1.931(10)	W(9B)-O(34B)	1.933(10)
W(10A)-O(34A)	1.884(10)	W(10B)-O(34B)	1.884(10)

Table S2 continued

W(10A)-O(35A)	1.885(10)	W(10B)-O(35B)	1.870(10)
W(11A)-O(35A)	1.948(10)	W(11B)-O(35B)	1.948(10)
W(11A)-O(33A)	1.974(10)	W(11B)-O(33B)	1.950(10)
W(11A)-O(28A)	1.822(10)	W(11B)-O(28B)	1.810 (11)
		average = 1.895 [1.792(10)-2.001(10)]	
W-O_e (O_e : edge-sharing oxygen)			
W(1A)-O(4A)	1.936(10)	W(1B)-O(4B)	1.927(10)
W(1A)-O(6A)	1.919(10)	W(1B)-O(6B)	1.947(10)
W(2A)-O(5A)	1.848(10)	W(2B)-O(5B)	1.832(10)
W(2A)-O(4A)	1.925(10)	W(2B)-O(4B)	1.901(9)
W(3A)-O(6A)	1.942(10)	W(3B)-O(6B)	1.948(10)
W(3A)-O(5A)	2.003(10)	W(3B)-O(5B)	2.004(11)
W(4A)-O(24A)	1.900(10)	W(4B)-O(24B)	1.916(10)
W(4A)-O(18A)	1.955(10)	W(4B)-O(18B)	1.937(10)
W(5A)-O(25A)	1.951(10)	W(5B)-O(25B)	1.949(9)
W(5A)-O(18A)	1.889(10)	W(5B)-O(18B)	1.904(10)
W(6A)-O(26A)	1.932(10)	W(6B)-O(26B)	1.928(10)
W(6A)-O(20A)	1.884(10)	W(6B)-O(20B)	1.884(10)
W(7A)-O(27A)	1.934(10)	W(7B)-O(27B)	1.942(10)
W(7A)-O(20A)	1.969(11)	W(7B)-O(20B)	1.981(11)
W(8A)-O(29A)	1.941(10)	W(8B)-O(29B)	1.918(10)
W(9A)-O(25A)	1.942(10)	W(9B)-O(25B)	1.942(10)
W(9A)-O(24A)	1.924(10)	W(9B)-O(24B)	1.917(10)
W(10A)-O(26A)	1.943(10)	W(10B)-O(26B)	1.927(10)
W(10A)-O(27A)	1.930(10)	W(10B)-O(27B)	1.948(10)
W(11A)-O(29A)	1.905(10)	W(11B)-O(29B)	1.910(10)
		average = 1.928 [1.832(10)-2.004(11)]	
W-O_a (oxygen coordinating to P atom)			
W(1A)-O(39A)	2.425(9)	W(1B)-O(39B)	2.429(9)
W(2A)-O(39A)	2.503(10)	W(2B)-O(39B)	2.490(9)
W(3A)-O(39A)	2.395(10)	W(3B)-O(39B)	2.424(10)
W(4A)-O(36A)	2.445(9)	W(4B)-O(36B)	2.447(9)
W(5A)-O(36A)	2.372(10)	W(5B)-O(36B)	2.378(10)
W(6A)-O(37A)	2.461(10)	W(6B)-O(37B)	2.486(10)
W(7A)-O(37A)	2.433(10)	W(7B)-O(37B)	2.445(10)

Table S2 continued

W(8A)-O(38A)	2.364(9)	W(8B)-O(38B)	2.378(9)
W(9A)-O(36A)	2.440(10)	W(9B)-O(36B)	2.438(9)
W(10A)-O(37A)	2.411(9)	W(10B)-O(37B)	2.409(9)
W(11A)-O(38A)	2.390(9)	W(11B)-O(38B)	2.392(9)
		average = 2.425 [2.364(9)-2.503(10)]	
P-O			
P(1A)-O(36A)	1.549(10)	P(1B)-O(36B)	1.547(10)
P(1A)-O(37A)	1.546(10)	P(1B)-O(37B)	1.523(10)
P(1A)-O(38A)	1.525(10)	P(1B)-O(38B)	1.514(10)
P(1A)-O(39A)	1.536(10)	P(1B)-O(39B)	1.523(9)
		average = 1.533 [1.523(9)-1.547(10)]	
O-P-O			
O(38A)-P(1A)-O(36A)	110.9(6)	O(38B)-P(1B)-O(36B)	110.5(5)
O(38A)-P(1A)-O(39A)	109.7(6)	O(38B)-P(1B)-O(39B)	109.5(6)
O(36A)-P(1A)-O(39A)	109.1(6)	O(36B)-P(1B)-O(39B)	109.3(5)
O(38A)-P(1A)-O(37A)	109.7(5)	O(38B)-P(1B)-O(37B)	109.5(6)
O(36A)-P(1A)-O(37A)	108.0(6)	O(36B)-P(1B)-O(37B)	108.5(6)
O(39A)-P(1A)-O(37A)	109.3(5)	O(39B)-P(1B)-O(37B)	109.5(5)
		average = 109.5 [108.0(6)-110.9(6)]	

Table S3 Bond valence sum (BVS) calculations of W, Hf, O and P atoms for **1** in Et_2NH_2-**1**

O(1A)	1.703	O(1B)	1.887	W(1A)	5.917
O(2A)	1.722	O(2B)	1.712	W(2A)	5.946
O(3A)	1.774	O(3B)	1.759	W(3A)	6.208
O(4A)	1.887	O(4B)	2.006	W(4A)	6.009
O(5A)	1.993	O(5B)	1.987	W(5A)	5.893
O(6A)	1.911	O(6B)	1.885	W(6A)	6.294
O(7A)	2.033	O(7B)	2.073	W(7A)	6.176
O(8A)	1.992	O(8B)	2.000	W(8A)	6.097
O(9A)	2.059	O(9B)	2.035	W(9A)	6.113
O(10A)	1.985	O(10B)	1.941	W(10A)	6.121
O(11A)	1.986	O(11B)	1.947	W(11A)	6.011
O(12A)	2.067	O(12B)	2.078		
O(13A)	1.694	O(13B)	1.774	W(1B)	6.296
O(14A)	1.605	O(14B)	1.592	W(2B)	6.040
O(15A)	1.842	O(15B)	1.793	W(3B)	6.101
O(16A)	1.803	O(16B)	1.635	W(4B)	6.053
O(17A)	1.717	O(17B)	1.822	W(5B)	5.938
O(18A)	1.881	O(18B)	1.941	W(6B)	6.157
O(19A)	2.051	O(19B)	2.025	W(7B)	6.026
O(20A)	2.044	O(20B)	2.005	W(8B)	6.224
O(21A)	2.035	O(21B)	2.017	W(9B)	5.842
O(22A)	1.930	O(22B)	1.956	W(10B)	6.319
O(23A)	1.983	O(23B)	1.949	W(11B)	6.094
O(24A)	2.003	O(24B)	1.973		
O(25A)	1.772	O(25B)	1.827	O(1M)	1.170
O(26A)	1.858	O(26B)	1.987	O(2M)	1.160
O(27A)	1.931	O(27B)	1.859		
O(28A)	1.902	O(28B)	1.945	Hf(1A)	4.180
O(29A)	1.952	O(29B)	2.019	Hf(1B)	4.146
O(30A)	1.769	O(30B)	1.726		
O(31A)	1.803	O(31B)	1.842	P(1A)	4.984
O(32A)	1.803	O(32B)	1.703	P(1B)	5.032

Table S3 continued

(33A)	2.009	O(33B)	2.002	O(1WA)	0.476
O(34A)	2.072	O(34B)	2.047	O(1WB)	0.490
O(35A)	1.995	O(35B)	2.065		
O(36A)	2.013	O(36B)	1.961		
O(37A)	1.929	O(37B)	1.958		
O(38A)	1.884	O(38B)	2.099		
O(39A)	1.976	O(39B)	1.955		

Table S4 Bond valence sum (BVS) calculations of W, Zr, O and P atoms for **2** in Et_2NH_2-**2**

O(1A)	1.807	O(1B)	1.774	W(1A)	6.160
O(2A)	1.857	O(2B)	1.778	W(2A)	6.225
O(3A)	1.764	O(3B)	1.778	W(3A)	6.169
O(4A)	1.929	O(4B)	2.018	W(4A)	6.220
O(5A)	1.998	O(5B)	2.049	W(5A)	6.152
O(6A)	1.929	O(6B)	1.842	W(6A)	6.060
O(7A)	2.054	O(7B)	2.071	W(7A)	6.166
O(8A)	2.038	O(8B)	2.018	W(8A)	6.088
O(9A)	2.100	O(9B)	2.029	W(9A)	6.107
O(10A)	1.977	O(10B)	1.942	W(10A)	6.025
O(11A)	1.961	O(11B)	1.954	W(11A)	6.150
O(12A)	2.031	O(12B)	2.071		
O(13A)	1.807	O(13B)	1.754	W(1B)	6.166
O(14A)	1.708	O(14B)	1.736	W(2B)	6.189
O(15A)	1.774	O(15B)	1.892	W(3B)	6.089
O(16A)	1.783	O(16B)	1.703	W(4B)	6.075
O(17A)	1.722	O(17B)	1.764	W(5B)	6.092
O(18A)	1.981	O(18B)	1.983	W(6B)	6.213
O(19A)	2.005	O(19B)	2.006	W(7B)	6.118
O(20A)	1.962	O(20B)	1.934	W(8B)	6.132
O(21A)	2.001	O(21B)	2.005	W(9B)	6.013
O(22A)	1.916	O(22B)	1.923	W(10B)	6.131
O(23A)	2.048	O(23B)	1.909	W(11B)	6.178
O(24A)	2.028	O(24B)	2.004		
O(25A)	1.847	O(25B)	1.852	O(1M)	1.100
O(26A)	1.892	O(26B)	1.944	O(2M)	1.106
O(27A)	1.921	O(27B)	1.854		
O(28A)	1.891	O(28B)	1.937	Zr(1A)	3.936
O(29A)	1.970	O(29B)	2.016	Zr(1B)	3.934
O(30A)	1.774	O(30B)	1.764		
O(31A)	1.680	O(31B)	1.745	P(1A)	4.940
O(32A)	1.769	O(32B)	1.712	P(1B)	5.108

Table S4 continued

O(33A)	2.069	O(33B)	2.026	O(1WA)	0.437
O(34A)	2.056	O(34B)	2.051	O(1WB)	0.455
O(35A)	2.010	O(35B)	2.055		
O(36A)	1.977	O(36B)	1.979		
O(37A)	1.952	O(37B)	2.009		
O(38A)	1.860	O(38B)	1.886		
O(39A)	1.978	O(39B)	2.006		