Syntheses and X-Ray Crystal Structures of Zirconium(IV) and Hafnium(IV) Complexes Containing Monovacant Wells-Dawson and Keggin Polyoxotungstates

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Figure S2. FTIR spectra in the polyoxoanion region (1800–400 cm⁻¹), measured as KBr disks, of (a) **Et₂NH₂-3**, (b) **Et₂NH₂-4**, and (c) (Et₂NH₂)₆H[α-PW₁₁O₃₉]·3H₂O.

Table S1. Selected bond lengths around Zr and Hf centers in **K-1** and **K-2**.

Zr-O distance (Å) for K-1		Hf-O distance (Å) for K-2	
Zr(1)-O1L	2.201(9)	Hf(1)-O1L	2.179(13)
Zr(1)-O2L	2.209(8)	Hf(1)-O2L	2.187(12)
Zr(1)-O3L	2.172(9)	Hf(1)-O3L	2.158(12)
Zr(1)-O4L	2.229(8)	Hf(1)-O4L	2.219(13)
Zr(1)-O1LA	2.201(9)	Hf(1)-O1LA	2.179(13)
Zr(1)-O2LA	2.209(8)	Hf(1)-O2LA	2.187(12)
Zr(1)-O3LA	2.172(9)	Hf(1)-O3LA	2.158(12)
Zr(1)-O4LA	2.229(8)	Hf(1)-O4LA	2.219(13)
O1L-O2L	2.671	O1L-O2L	2.630
O2L-O3L	2.678	O2L-O3L	2.657
O3L-O4L	2.566	O3L-O4L	2.553
O4L-O1L	2.648	O4L-O1L	2.640
O1LA-O2LA	2.671	O1LA-O2LA	2.630
O2LA-O3LA	2.678	O2LA-O3LA	2.657
O3LA-O4LA	2.566	O3LA-O4LA	2.553
O4LA-O1LA	2.648	O4LA-O1LA	2.640

Table S2. Bond lengths (Å) and angles (°) for **K-1**.

Cap W (15, 16, 17)	
M-O(terminal)	1.717 [1.709(9)- 1.725(9)]
M-O(M cap)	1.936 [1.903(8)- 1.980(8)]
M-O(W belt)	1.883 [1.859(9)- 1.907(9)]
M-O(P)	2.372 [2.329(9)- 2.397(8)]

Belt W (9-14)	Belt W (3-8)
M-O(terminal)	1.724 [1.714(9)- 1.741(9)]
M-O(M cap)	1.955 [1.898(9)- 2.012(9)]
M-O(belt edge)	1.917 [1.896(9)- 1.941(9)]
M-O(belt same)	1.898 [1.858(9)- 1.937(8)]
M-O(between)	1.850 [1.797(8)- 1.911(9)]
M-O(P)	2.358 [2.334(9)- 2.377(9)]

Cap W (1, 2)		
M - O(terminal)	O(1)-W(1)	1.719(8)
	O(3)-W(2)	1.719(9)

M – O (W cap)	O(2)-W(1)	1.945(9)
	O(2)-W(2)	1.929(8)
	O(1L)-W(1)	1.793(9)
	O(2L)-W(2)	1.801(8)

M – O (W belt)	O(4)-W(1)	2.031(8)
	O(7)-W(1)	1.895(8)
	O(5)-W(2)	2.039(9)
	O(6)-W(2)	1.906(8)

M - O _P	O(8)-W(1)	2.265(8)
	O(8)-W(2)	2.260(9)

Zr side (P1)	W ₃ cap side (P2)
P-O distance	1.542[1.535(9)- 1.556(8)]
O-P-O angle	109.5[107.8(5)- 111.3(5)]

Table S3. Bond lengths (Å) and angles (°) for **K-2**.

Cap W (15, 16, 17)		
M-O(terminal)	1.720 [1.711(13)- 1.737(15)]	
M-O(M cap)	1.934 [1.902(14)- 1.978(13)]	
M-O(W belt)	1.886 [1.852(13)- 1.923(13)]	
M-O(P)	2.374 [2.348(13)- 2.396(13)]	

	Belt W (9-14)	Belt W (3-8)
M-O(terminal)	1.719 [1.694(15)- 1.737(16)]	1.724 [1.716(13)- 1.732(14)]
M-O(M cap)	1.954 [1.893(13)- 2.014(13)]	1.845 [1.767(12)- 1.928(13)]
M-O(belt edge)	1.924 [1.908(13)- 1.959(13)]	1.915 [1.881(12)- 1.949(13)]
M-O(belt same)	1.902 [1.883(14)- 1.926(13)]	1.904 [1.883(12)- 1.926(12)]
M-O(between)	1.847 [1.787(13)- 1.918(12)]	1.994 [1.895(12)- 2.118(13)]
M-O(P)	2.363 [2.330(12)- 2.392(13)]	2.348 [2.325(12)- 2.378(12)]

Cap W (1, 2)		
M - O(terminal)	O(1)-W(1)	1.741(13)
	O(3)-W(2)	1.736(13)
M – O (W cap)	O(2)-W(1)	1.950(13)
	O(2)-W(2)	1.940(12)
	O(1L)-W(1)	1.794(12)
	O(2L)-W(2)	1.809(12)
M – O (W belt)	O(4)-W(1)	2.037(12)
	O(7)-W(1)	1.884(13)
	O(5)-W(2)	2.037(12)
	O(6)-W(2)	1.925(12)
M - O _P	O(8)-W(1)	2.268(12)
	O(8)-W(2)	2.248(12)

	Hf side (P1)	W ₃ cap side (P2)
P-O distance	1.544[1.530(12)- 1.559(12)]	1.542 [1.521(14)- 1.573(14)]
O-P-O angle	109.5[107.3(7)- 111.0(7)]	109.4[106.2(7)- 112.5(8)]

Table S4. Bond balance sums for **K-1**.

	BVS		BVS
Zr1	3.812	O18	1.680
W1	6.219	O19	2.010
W2	6.189	O20	1.694
W3	6.076	O21	1.836
W4	6.144	O22	1.888
W5	6.194	O23	1.876
W6	6.133	O24	2.091
W7	6.124	O25	2.083
W8	6.213	O26	2.080
W9	6.187	O27	2.041
W10	6.128	O28	1.977
W11	6.185	O29	2.083
W12	6.196	O30	2.120
W13	6.111	O31	1.731
W14	6.172	O32	2.018
W15	6.108	O33	1.676
W16	6.188	O34	2.091
W17	6.030	O35	1.722
P1	4.896	O36	1.995
P2	4.921	O37	1.694
O1L	1.876	O38	2.123
O2L	1.836	O39	1.609
O3L	2.001	O40	1.989
O4L	1.931	O41	1.685
O1	1.708	O42	1.885
O2	1.895	O43	1.857
O3	1.708	O44	1.878
O4	1.966	O45	2.005
O5	1.934	O46	2.007
O6	2.025	O47	2.016
O7	2.066	O48	2.089
O8	1.965	O49	1.944
O9	2.100	O50	1.931
O10	1.726	O51	2.046
O11	2.074	O52	1.712
O12	1.640	O53	1.968
O13	2.069	O54	1.754
O14	1.680	O55	1.882
O15	2.010	O56	1.680
O16	1.698	O57	1.869
O17	2.097		

Table S5. Bond balance sums for **K-2**.

	BVS		BVS
Hf1	4.164	O18	1.685
W1	6.121	O19	2.078
W2	6.021	O20	1.676
W3	5.939	O21	1.874
W4	6.159	O22	1.877
W5	6.165	O23	1.826
W6	6.089	O24	2.103
W7	6.085	O25	2.066
W8	6.200	O26	2.058
W9	6.116	O27	2.017
W10	6.146	O28	2.002
W11	6.102	O29	2.067
W12	6.083	O30	2.072
W13	6.225	O31	1.627
W14	6.314	O32	1.983
W15	6.210	O33	1.680
W16	6.103	O34	2.097
W17	5.977	O35	1.717
P1	4.872	O36	1.915
P2	4.908	O37	1.712
O1L	1.923	O38	2.088
O2L	1.857	O39	1.689
O3L	1.989	O40	1.993
O4L	1.975	O41	1.827
O1	1.609	O42	1.863
O2	1.855	O43	1.874
O3	1.631	O44	1.846
O4	1.974	O45	2.000
O5	1.935	O46	2.016
O6	1.998	O47	2.021
O7	2.064	O48	2.041
O8	1.966	O49	1.927
O9	2.072	O50	1.961
O10	1.685	O51	2.051
O11	2.010	O52	1.740
O12	1.649	O53	1.978
O13	2.083	O54	1.745
O14	1.698	O55	1.884
O15	1.958	O56	1.627
O16	1.722	O57	1.894
O17	2.067		

Table S6. Selected bond lengths around Zr and Hf centers in **Et₂NH₂-3** and **Et₂NH₂-4**.

Zr-O distance (Å) for Et₂NH₂-3		Hf-O distance (Å) for Et₂NH₂-4	
Zr(1)-O1AL	2.224(19)	Hf(1)-O1AL	2.205(15)
Zr(1)-O2AL	2.16(2)	Hf(1)-O2AL	2.200(16)
Zr(1)-O3AL	2.206(19)	Hf(1)-O3AL	2.222(16)
Zr(1)-O4AL	2.18(2)	Hf(1)-O4AL	2.170(19)
Zr(1)-O1BL	2.23(3)	Hf(1)-O1BL	2.197(17)
Zr(1)-O2BL	2.199(19)	Hf(1)-O2BL	2.168(16)
Zr(1)-O3BL	2.20(2)	Hf(1)-O3BL	2.229(15)
Zr(1)-O4BL	2.24(2)	Hf(1)-O4BL	2.199(16)
O1AL-O2AL	2.573	O1AL-O2AL	2.578
O2AL-O3AL	2.634	O2AL-O3AL	2.641
O3AL-O4AL	2.634	O3AL-O4AL	2.657
O4AL-O1AL	2.693	O4AL-O1AL	2.664
O1BL-O2BL	2.623	O1BL-O2BL	2.572
O2BL-O3BL	2.684	O2BL-O3BL	2.627
O3BL-O4BL	2.606	O3BL-O4BL	2.655
O4BL-O1BL	2.711	O4BL-O1BL	2.643
Zr(2)-O1C'L	2.24(2)	Hf(2)-O1CL	2.157(15)
Zr(2)-O2C'L	2.18(2)	Hf(2)-O2CL	2.197(16)
Zr(2)-O3C'L	2.22(2)	Hf(2)-O3CL	2.217(16)
Zr(2)-O4C'L	2.19(2)	Hf(2)-O4CL	2.160(17)
Zr(2)-O1D'L	2.174(18)	Hf(2)-O1DL	2.227(16)
Zr(2)-O2D'L	2.219(19)	Hf(2)-O2DL	2.183(16)
Zr(2)-O3D'L	2.23(2)	Hf(2)-O3DL	2.227(15)
Zr(2)-O4D'L	2.20(2)	Hf(2)-O4DL	2.177(16)
O1C'L-O2C'L	2.595	O1CL-O2CL	2.576
O2C'L-O3C'L	2.623	O2CL-O3CL	2.636
O3C'L-O4C'L	2.711	O3CL-O4CL	2.596
O4C'L-O1C'L	2.634	O4CL-O1CL	2.639
O1D'L-O2D'L	2.553	O1DL-O2DL	2.586
O2D'L-O3D'L	2.637	O2DL-O3DL	2.684
O3D'L-O4D'L	2.664	O3DL-O4DL	2.651
O4D'L-O1D'L	2.672	O4DL-O1DL	2.639

Table S7. Bond lengths (Å) and angles (°) for **Et₂NH₂-3**.

A	Cap W (3, 4, 9)	Cap(Zr site) W(6, 7)
M-O(terminal)	1.73[1.73(3) - 1.74(3)]	1.73[1.71(2) - 1.74(2)]
M-O(M cap)	1.93 [1.84(2) - 1.97(3)]	1.87[1.800(19) - 1.95(2)]
M-O(W belt)	1.88 [1.83(3) - 1.93(2)]	1.99[1.92(2) - 2.07(2)]
M-O(P)	2.40[2.35(2) -2.44(2)]	2.337[2.331(19)- 2.342(19)]
Belt W (1, 2, 5, 8, 10, 11)		
M-O(terminal)	1.73 [1.68(3)- 1.76(2)]	
M-O(W ₃ cap)	1.99 [1.90(2)- 2.06(3)]	
M-O(belt edge)	1.92 [1.86(2)- 1.98(2)]	
M-O(belt same)	1.91 [1.86(2)- 1.96(2)]	
M-O(Zr cap)	1.84 [1.771(19)- 1.90(2)]	
M-O(P)	2.42 [2.36(2)- 2.44(2)]	
B	Cap W (3, 4, 9)	Cap(Zr site) W(6, 7)
M-O(terminal)	1.73[1.72(2) - 1.73(3)]	1.73[1.72(2) - 1.74(2)]
M-O(M cap)	1.91 [1.87(3) - 1.97(3)]	1.84[1.74(2) - 1.92(2)]
M-O(W belt)	1.87 [1.81(2) - 1.96(2)]	1.98[1.928(19) - 2.04(3)]
M-O(P)	2.42[2.39(2) -2.45(2)]	2.30[2.272(19)- 2.32(2)]
Belt W (1, 2, 5, 8, 10, 11)		
M-O(terminal)	1.70 [1.68(3)- 1.74(2)]	
M-O(W ₃ cap)	1.99 [1.92(2)- 2.04(2)]	
M-O(belt edge)	1.93 [1.89(2)- 1.96(2)]	
M-O(belt same)	1.90 [1.84(3)- 1.95(3)]	
M-O(Zr cap)	1.84 [1.75(2)- 1.91(3)]	
M-O(P)	2.40 [2.36(2)- 2.44(2)]	

Table S7-continued.

C'	Cap W (3, 4, 9)	Cap(Zr site) W(6, 7)
M-O(terminal)	1.71[1.70(2) - 1.72(2)]	1.75[1.73(2) - 1.77(2)]
M-O(M cap)	1.91 [1.88(2) - 1.95(2)]	1.86[1.78(2) - 1.920(19)]
M-O(W belt)	1.89 [1.83(3) - 1.96(2)]	1.97[1.920(19) - 2.03(2)]
M-O(P)	2.42[2.36(2) -2.45(2)]	2.36[2.35(2)- 2.37(2)]

	Belt W (1, 2, 5, 8, 10, 11)
M-O(terminal)	1.73 [1.67(2)- 1.79(2)]
M-O(W ₃ cap)	1.98 [1.89(2)- 2.11(2)]
M-O(belt edge)	1.92 [1.89(2)- 1.937(19)]
M-O(belt same)	1.91 [1.86(2)- 1.95(2)]
M-O(Zr cap)	1.84 [1.77(2)- 1.90(2)]
M-O(P)	2.44 [2.428(19)- 2.451(19)]

D'	Cap W (3, 4, 9)	Cap(Zr site) W(6, 7)
M-O(terminal)	1.73[1.721(18) - 1.74(2)]	1.72[1.71(2) - 1.72(2)]
M-O(M cap)	1.92 [1.891(18) - 1.96(2)]	1.87[1.78(2) - 1.959(18)]
M-O(W belt)	1.89 [1.82(2) - 1.96(2)]	1.97[1.89(2) - 2.052(19)]
M-O(P)	2.42[2.348(18) -2.46(2)]	2.33[2.303(19)- 2.35(2)]

	Belt W (1, 2, 5, 8, 10, 11)
M-O(terminal)	1.72 [1.70(2)- 1.75(3)]
M-O(W ₃ cap)	1.99 [1.90(2)- 2.08(2)]
M-O(belt edge)	1.93 [1.89(2)- 1.98(2)]
M-O(belt same)	1.91 [1.89(2)- 1.94(2)]
M-O(Zr cap)	1.84 [1.754(18)- 1.92 (2)]
M-O(P)	2.44 [2.42 (2)- 2.483(19)]

Table S8. Bond lengths (Å) and angles (°) for **Et₂NH₂-4**.

A	Cap W (3, 4, 9)	Cap(Hf site) W(6, 7)
M-O(terminal)	1.72[1.70(2) - 1.73(2)]	1.705[1.704(18) - 1.706(17)]
M-O(M cap)	1.91 [1.86(2) - 1.98(2)]	1.86[1.789(18) - 1.936(18)]
M-O(W belt)	1.87 [1.81(2) - 1.96(2)]	2.00[1.929(17) - 2.073(19)]
M-O(P)	2.41[2.35(2) -2.441(17)]	2.315[2.315(16)- 2.315(16)]
Belt W (1, 2, 5, 8, 10, 11)		
M-O(terminal)	1.72 [1.68(2)- 1.75(3)]	
M-O(W ₃ cap)	2.00 [1.922(19)- 2.10(2)]	
M-O(belt edge)	1.93 [1.89(2)- 1.97(2)]	
M-O(belt same)	1.90 [1.89(2)- 1.91(2)]	
M-O(Hf cap)	1.82 [1.770(15)- 1.893(17)]	
M-O(P)	2.42 [2.40(2)- 2.436(18)]	
B	Cap W (3, 4, 9)	Cap(Hf site) W(6, 7)
M-O(terminal)	1.70 [1.69(3) - 1.71(3)]	1.761[1.758(17) - 1.763(19)]
M-O(M cap)	1.90 [1.85(2) - 1.98(2)]	1.848[1.774(17) - 1.921(16)]
M-O(W belt)	1.88 [1.84(2) - 1.91(3)]	1.99[1.91(2) - 2.07(2)]
M-O(P)	2.44 [2.436(15) -2.44 (2)]	2.302[2.268(16)- 2.336(16)]
Belt W (1, 2, 5, 8, 10, 11)		
M-O(terminal)	1.70 [1.66(2)- 1.75(2)]	
M-O(W ₃ cap)	1.98 [1.93(3)- 2.061(18)]	
M-O(belt edge)	1.93 [1.89(2)- 1.942(19)]	
M-O(belt same)	1.90 [1.86(2)- 1.94(2)]	
M-O(Hf cap)	1.85 [1.783(16)- 1.94(2)]	
M-O(P)	2.41 [2.36(2)- 2.448(18)]	

Table S8-continued.

C	Cap W (3, 4, 9)	Cap(Hf site) W(6, 7)
M-O(terminal)	1.724 [1.706(19) - 1.745(19)]	1.721[1.717(18) - 1.725(17)]
M-O(M cap)	1.912 [1.890(17) - 1.945(18)]	1.876[1.790(17) - 1.960(16)]
M-O(W belt)	1.89 [1.835(18) - 1.927(16)]	1.986[1.922(16) - 2.049(16)]
M-O(P)	2.409 [2.347(16) -2.449(15)]	2.322[2.291(14)- 2.353(14)]

	Belt W (1, 2, 5, 8, 10, 11)
M-O(terminal)	1.722 [1.684(18)- 1.759(18)]
M-O(W ₃ cap)	1.973 [1.906(16)- 2.072(18)]
M-O(belt edge)	1.922 [1.896(18)- 1.961(19)]
M-O(belt same)	1.907 [1.863(17)- 1.949(16)]
M-O(Hf cap)	1.835 [1.773(15)- 1.897(15)]
M-O(P)	2.431 [2.402(16)- 2.448(16)]

D	Cap W (3, 4, 9)	Cap(Hf site) W(6, 7)
M-O(terminal)	1.71 [1.68(2)- 1.73(2)]	1.724[1.719(14)- 1.728(18)]
M-O(M cap)	1.91 [1.882(19) - 1.930(19)]	1.843[1.775(16) - 1.915(18)]
M-O(W belt)	1.90 [1.823(17) - 1.942(19)]	1.961[1.897(17) - 2.018(17)]
M-O(P)	2.417 [2.358(17) 2.461(16)]	2.310[2.294(16)- 2.326(15)]

	Belt W (1, 2, 5, 8, 10, 11)
M-O(terminal)	1.708 [1.693(19)- 1.728(19)]
M-O(W ₃ cap)	1.972 [1.929(19)- 2.077(17)]
M-O(belt edge)	1.914 [1.85(2)- 1.970(19)]
M-O(belt same)	1.846 [1.758(16)- 1.917(18)]
M-O(Hf cap)	1.905 [1.867(16)- 1.958(16)]
M-O(P)	2.429 [2.415(16)- 2.445(18)]

Table S9. Bond balance sums for **Et₂NH₂-3**.

	BVS		BVS
Zr1	3.793	O10A	2.098
W1A	6.038	O11A	1.658
W2A	5.708	O12A	2.012
W3A	5.853	O13A	1.570
W4A	6.307	O14A	2.050
W5A	5.884	O15A	1.750
W6A	6.010	O16A	1.962
W7A	6.012	O17A	1.613
W8A	6.255	O18A	2.039
W9A	6.110	O19A	1.847
W10A	6.029	O20A	1.924
W11A	6.299	O21A	1.981
P1A	4.739	O22A	1.909
O1AL	1.933	O23A	1.945
O2AL	1.834	O24A	1.832
O3AL	1.807	O25A	1.930
O4AL	1.878	O26A	2.057
O1A	1.658	O27A	1.945
O2A	2.070	O28A	2.071
O3A	1.529	O29A	1.957
O4A	1.897	O30A	2.022
O5A	1.910	O31A	1.613
O6A	1.984	O32A	1.882
O7A	2.010	O33A	1.529
O8A	1.984	O34A	1.959
O9A	1.658	O35A	1.898

Table S9-continued.

	BVS		BVS
W1B	6.304	O10B	2.127
W2B	6.114	O11B	1.703
W3B	6.390	O12B	2.045
W4B	6.290	O13B	1.708
W5B	6.021	O14B	2.106
W6B	6.089	O15B	1.613
W7B	6.323	O16B	2.097
W8B	6.357	O17B	1.703
W9B	6.210	O18B	1.934
W10B	6.288	O19B	1.898
W11B	5.990	O20B	1.872
P1B	4.609	O21B	1.917
O1BL	1.890	O22B	1.918
O2BL	2.051	O23B	2.011
O3BL	1.744	O24B	2.002
O4BL	2.043	O25B	2.075
O1B	1.898	O26B	2.181
O2B	2.011	O27B	1.934
O3B	1.613	O28B	1.822
O4B	2.052	O29B	2.146
O5B	2.017	O30B	1.945
O6B	1.855	O31B	1.658
O7B	1.880	O32B	1.995
O8B	1.882	O33B	1.847
O9B	1.658	O34B	2.068
		O35B	1.898

Table S9-continued.

	BVS		BVS
Zr2	3.773	O10C'	2.070
W1C'	6.024	O11C'	1.703
W2C'	5.780	O12C'	2.016
W3C'	6.126	O13C'	1.703
W4C'	6.491	O14C'	2.100
W5C'	6.032	O15C'	1.488
W6C'	5.849	O16C'	2.006
W7C'	6.162	O17C'	1.658
W8C'	6.131	O18C'	2.039
W9C'	6.036	O19C'	1.658
W10C'	6.317	O20C'	1.953
W11C'	6.101	O21C'	2.023
P1C'	5.325	O22C'	2.133
O1C'L	1.918	O23C'	2.061
O2C'L	1.916	O24C'	1.984
O3C'L	1.789	O25C'	2.020
O4C'L	1.941	O26C'	2.038
O1C'	1.613	O27C'	2.002
O2C'	2.077	O28C'	1.913
O3C'	1.410	O29C'	2.082
O4C'	1.926	O30C'	2.002
O5C'	1.859	O31C'	1.750
O6C'	2.068	O32C'	1.934
O7C'	1.936	O33C'	1.798
O8C'	1.966	O34C'	1.957
O9C'	1.798	O35C'	1.949

Table S9-continued.

	BVS		BVS
W1D'	6.084	O10D'	2.049
W2D'	6.158	O11D'	1.658
W3D'	6.086	O12D'	1.997
W4D'	6.013	O13D'	1.570
W5D'	5.814	O14D'	2.071
W6D'	6.155	O15D'	1.703
W7D'	6.150	O16D'	1.923
W8D'	5.858	O17D'	1.750
W9D'	6.103	O18D'	1.984
W10D'	6.095	O19D'	1.570
W11D'	5.983	O20D'	1.955
P1D'	5.282	O21D'	2.113
O1D'L	1.931	O22D'	2.072
O2D'L	2.009	O23D'	2.043
O3D'L	1.742	O24D'	1.971
O4D'L	1.927	O25D'	1.937
O1D'	1.750	O26D'	2.016
O2D'	2.041	O27D'	1.959
O3D'	1.798	O28D'	1.952
O4D'	1.944	O29D'	2.041
O5D'	1.846	O30D'	1.938
O6D'	1.860	O31D'	1.613
O7D'	1.987	O32D'	1.897
O8D'	1.937	O33D'	1.750
O9D'	1.698	O34D'	1.919
		O35D'	1.750

Table S10. Bond balance sums for **Et₂NH₂-4**.

	BVS		BVS
Hf1	4.022	O10A	2.127
W1A	6.047	O11A	1.703
W2A	6.027	O12A	2.017
W3A	6.218	O13A	1.703
W4A	6.389	O14A	2.109
W5A	6.159	O15A	1.769
W6A	6.148	O16A	1.989
W7A	6.126	O17A	1.778
W8A	6.260	O18A	2.035
W9A	6.275	O19A	1.898
W10A	6.214	O20A	1.998
W11A	5.778	O21A	2.023
P1A	4.917	O22A	1.951
O1AL	1.970	O23A	1.976
O2AL	1.988	O24A	2.010
O3AL	1.884	O25A	1.962
O4AL	1.915	O26A	2.095
O1A	1.812	O27A	2.017
O2A	2.058	O28A	1.982
O3A	1.570	O29A	2.123
O4A	1.875	O30A	2.072
O5A	1.937	O31A	1.658
O6A	1.990	O32A	1.757
O7A	1.943	O33A	1.658
O8A	1.966	O34A	1.880
O9A	1.798	O35A	1.570

Table S10-continued.

	BVS		BVS
W1B	6.221	O10B	2.152
W2B	5.932	O11B	1.798
W3B	6.519	O12B	1.959
W4B	6.370	O13B	1.812
W5B	6.116	O14B	2.103
W6B	5.956	O15B	1.537
W7B	6.060	O16B	1.994
W8B	6.059	O17B	1.516
W9B	6.163	O18B	1.959
W10B	6.041	O19B	1.750
W11B	6.403	O20B	1.966
P1B	4.788	O21B	1.942
O1BL	1.925	O22B	1.971
O2BL	1.981	O23B	1.958
O3BL	1.907	O24B	2.042
O4BL	1.974	O25B	2.068
O1B	1.898	O26B	2.101
O2B	2.011	O27B	1.876
O3B	1.570	O28B	1.828
O4B	1.968	O29B	2.107
O5B	1.909	O30B	1.934
O6B	1.920	O31B	1.847
O7B	1.900	O32B	1.978
O8B	1.984	O33B	1.703
O9B	1.750	O34B	2.041
		O35B	2.003

Table S10-continued.

	BVS		BVS
Hf2	4.087	O10C	2.108
W1C	6.316	O11C	1.694
W2C	5.968	O12C	2.010
W3C	6.228	O13C	1.635
W4C	6.200	O14C	2.095
W5C	5.934	O15C	1.680
W6C	6.008	O16C	1.967
W7C	6.161	O17C	1.717
W8C	5.980	O18C	2.016
W9C	5.995	O19C	1.533
W10C	6.086	O20C	1.931
W11C	6.279	O21C	2.008
P1C	5.066	O22C	2.004
O1CL	1.923	O23C	2.093
O2CL	1.980	O24C	2.003
O3CL	1.835	O25C	1.984
O4CL	1.967	O26C	2.035
O1C	1.877	O27C	1.962
O2C	2.074	O28C	1.991
O3C	1.658	O29C	2.074
O4C	1.973	O30C	1.968
O5C	1.857	O31C	1.592
O6C	1.904	O32C	1.894
O7C	2.008	O33C	1.717
O8C	2.003	O34C	2.014
O9C	1.769	O35C	1.769

Table S10-continued.

	BVS		BVS
W1D	6.348	O10D	2.064
W2D	6.201	O11D	1.750
W3D	6.593	O12D	1.954
W4D	5.975	O13D	1.667
W5D	5.967	O14D	2.057
W6D	6.273	O15D	1.708
W7D	6.341	O16D	2.075
W8D	6.127	O17D	1.667
W9D	5.934	O18D	2.015
W10D	6.209	O19D	1.817
W11D	6.157	O20D	1.945
P1D	4.965	O21D	2.013
O1DL	1.985	O22D	1.961
O2DL	2.061	O23D	2.025
O3DL	1.871	O24D	2.001
O4DL	2.000	O25D	2.011
O1D	1.754	O26D	2.040
O2D	2.093	O27D	1.909
O3D	1.832	O28D	1.956
O4D	1.938	O29D	2.095
O5D	1.771	O30D	1.994
O6D	2.066	O31D	1.658
O7D	2.069	O32D	1.903
O8D	2.012	O33D	1.759
O9D	1.898	O34D	1.951
		O35D	1.731

Table S11. The selected bond angles around Zr and Hf centers in complexes **1** and **2**.

K-1 (°)			
O(1L)-Zr(1)-O(2L)	74.5(3)	O(3L)-Zr(1)-O(1LA)	80.6(3)
O(1L)-Zr(1)-O(3L)	114.4(3)	O(3L)-Zr(1)-O(2LA)	146.1(3)
O(1L)-Zr(1)-O(4L)	73.4(3)	O(3L)-Zr(1)-O(3LA)	137.0(5)
O(1L)-Zr(1)-O(1LA)	140.3(4)	O(3L)-Zr(1)-O(4LA)	75.7(3)
O(1L)-Zr(1)-O(2LA)	74.5(3)	O(4L)-Zr(1)-O(1LA)	144.3(3)
O(1L)-Zr(1)-O(3LA)	80.6(3)	O(4L)-Zr(1)-O(2LA)	139.5(3)
O(1L)-Zr(1)-O(4LA)	144.3(3)	O(4L)-Zr(1)-O(3LA)	75.7(3)
O(2L)-Zr(1)-O(3L)	75.3(3)	O(4L)-Zr(1)-O(4LA)	78.6(5)
O(2L)-Zr(1)-O(4L)	117.3(3)	O(1LA)-Zr(1)-O(2LA)	74.5(3)
O(2L)-Zr(1)-O(1LA)	74.5(3)	O(1LA)-Zr(1)-O(3LA)	114.4(3)
O(2L)-Zr(1)-O(2LA)	76.1(5)	O(1LA)-Zr(1)-O(4LA)	73.4(3)
O(2L)-Zr(1)-O(3LA)	146.1(3)	O(2LA)-Zr(1)-O(3LA)	75.3(3)
O(2L)-Zr(1)-O(4LA)	139.5(3)	O(2LA)-Zr(1)-O(4LA)	117.3(3)
O(3L)-Zr(1)-O(4L)	71.3(3)	O(3LA)-Zr(1)-O(4LA)	71.3(3)
K-2 (°)			
O(1L)-Hf(1)-O(2L)	74.1(5)	O(3L)-Hf(1)-O(1LA)	80.5(5)
O(1L)-Hf(1)-O(3L)	114.0(4)	O(3L)-Hf(1)-O(2LA)	145.3(5)
O(1L)-Hf(1)-O(4L)	73.8(5)	O(3L)-Hf(1)-O(3LA)	137.7(7)
O(1L)-Hf(1)-O(1LA)	140.9(7)	O(3L)-Hf(1)-O(4LA)	75.9(4)
O(1L)-Hf(1)-O(2LA)	75.2(5)	O(4L)-Hf(1)-O(1LA)	143.5(5)
O(1L)-Hf(1)-O(3LA)	80.5(5)	O(4L)-Hf(1)-O(2LA)	140.5(5)
O(1L)-Hf(1)-O(4LA)	143.5(5)	O(4L)-Hf(1)-O(3LA)	75.9(4)
O(2L)-Hf(1)-O(3L)	75.4(5)	O(4L)-Hf(1)-O(4LA)	77.1(6)
O(2L)-Hf(1)-O(4L)	117.7(4)	O(1LA)-Hf(1)-O(2LA)	74.1(5)
O(2L)-Hf(1)-O(1LA)	75.2(5)	O(1LA)-Hf(1)-O(3LA)	114.0(4)
O(2L)-Hf(1)-O(2LA)	75.5(6)	O(1LA)-Hf(1)-O(4LA)	73.8(5)
O(2L)-Hf(1)-O(3LA)	145.3(5)	O(2LA)-Hf(1)-O(3LA)	75.4(5)
O(2L)-Hf(1)-O(4LA)	140.5(5)	O(2LA)-Hf(1)-O(4LA)	117.7(4)
O(3L)-Hf(1)-O(4L)	71.3(5)	O(3LA)-Hf(1)-O(4LA)	71.3(5)

Table S12. The selected bond angles around Zr and Hf centers in complexes **3** and **4**.

Et₂NH₂-3 (°)			
O(1AL)-Zr(1)-O(2AL)	71.8(8)	O(3AL)-Zr(1)-O(1BL)	80.0(8)
O(1AL)-Zr(1)-O(3AL)	116.0(8)	O(2BL)-Zr(1)-O(3AL)	146.9(8)
O(1AL)-Zr(1)-O(4AL)	75.3(7)	O(3BL)-Zr(1)-O(3AL)	135.4(7)
O(1AL)-Zr(1)-O(1BL)	135.0(8)	O(3AL)-Zr(1)-O(4BL)	74.8(7)
O(1AL)-Zr(1)-O(2BL)	74.1(7)	O(4AL)-Zr(1)-O(1BL)	147.4(8)
O(1AL)-Zr(1)-O(3BL)	81.8(7)	O(4AL)-Zr(1)-O(2BL)	137.8(8)
O(1AL)-Zr(1)-O(4BL)	148.2(7)	O(4AL)-Zr(1)-O(3BL)	72.2(8)
O(2AL)-Zr(1)-O(3AL)	74.1(7)	O(4AL)-Zr(1)-O(4BL)	79.9(8)
O(2AL)-Zr(1)-O(4AL)	116.2(8)	O(1BL)-Zr(1)-O(2BL)	72.7(8)
O(2AL)-Zr(1)-O(1BL)	73.4(9)	O(1BL)-Zr(1)-O(3BL)	117.3(8)
O(2AL)-Zr(1)-O(2BL)	80.4(7)	O(1BL)-Zr(1)-O(4BL)	74.7(8)
O(2AL)-Zr(1)-O(3BL)	148.1(7)	O(2BL)-Zr(1)-O(3BL)	75.3(7)
O(2AL)-Zr(1)-O(4BL)	138.5(8)	O(2BL)-Zr(1)-O(4BL)	114.3(8)
O(3AL)-Zr(1)-O(4AL)	73.7(7)	O(3BL)-Zr(1)-O(4BL)	71.8(7)
O(1C'L)-Zr(2)-O(2C'L)	72.1(7)	O(3C'L)-Zr(2)-O(1D'L)	79.7(7)
O(1C'L)-Zr(2)-O(3C'L)	117.0(8)	O(3C'L)-Zr(2)-O(2D'L)	145.3(7)
O(1C'L)-Zr(2)-O(4C'L)	73.0(8)	O(3C'L)-Zr(2)-O(3D'L)	139.1(8)
O(1C'L)-Zr(2)-O(1D'L)	135.1(7)	O(3C'L)-Zr(2)-O(4D'L)	74.1(8)
O(1C'L)-Zr(2)-O(2D'L)	75.1(7)	O(4C'L)-Zr(2)-O(1D'L)	149.8(7)
O(1C'L)-Zr(2)-O(3D'L)	79.9(7)	O(4C'L)-Zr(2)-O(2D'L)	137.3(7)
O(1C'L)-Zr(2)-O(4D'L)	147.2(7)	O(4C'L)-Zr(2)-O(3D'L)	74.4(8)
O(2C'L)-Zr(2)-O(3C'L)	73.3(8)	O(4C'L)-Zr(2)-O(4D'L)	81.0(7)
O(2C'L)-Zr(2)-O(4C'L)	114.4(8)	O(1D'L)-Zr(2)-O(2D'L)	71.0(6)
O(2C'L)-Zr(2)-O(1D'L)	74.3(7)	O(1D'L)-Zr(2)-O(3D'L)	115.7(7)
O(2C'L)-Zr(2)-O(2D'L)	81.0(7)	O(1D'L)-Zr(2)-O(4D'L)	75.4(7)
O(2C'L)-Zr(2)-O(3D'L)	145.6(8)	O(2D'L)-Zr(2)-O(3D'L)	72.7(7)
O(2C'L)-Zr(2)-O(4D'L)	138.6(7)	O(2D'L)-Zr(2)-O(4D'L)	114.5(7)
O(3C'L)-Zr(2)-O(4C'L)	75.9(8)	O(3D'L)-Zr(2)-O(4D'L)	74.0(7)

Table S12-continued.

Et₂NH₂-4 (°)			
O(1AL)-Hf(1)-O(2AL)	71.6(6)	O(3AL)-Hf(1)-O(1BL)	80.9(6)
O(1AL)-Hf(1)-O(3AL)	116.1(6)	O(3AL)-Hf(1)-O(2BL)	147.1(6)
O(1AL)-Hf(1)-O(4AL)	75.1(6)	O(3AL)-Hf(1)-O(3BL)	137.1(6)
O(1AL)-Hf(1)-O(1BL)	134.9(6)	O(3AL)-Hf(1)-O(4BL)	74.0(6)
O(1AL)-Hf(1)-O(2BL)	73.8(6)	O(4AL)-Hf(1)-O(1BL)	148.3(6)
O(1AL)-Hf(1)-O(3BL)	81.1(6)	O(4AL)-Hf(1)-O(2BL)	136.8(6)
O(1AL)-Hf(1)-O(4BL)	148.9(6)	O(4AL)-Hf(1)-O(3BL)	72.9(6)
O(2AL)-Hf(1)-O(3AL)	73.3(6)	O(4AL)-Hf(1)-O(4BL)	80.3(7)
O(2AL)-Hf(1)-O(4AL)	115.6(7)	O(1BL)-Hf(1)-O(2BL)	72.2(6)
O(2AL)-Hf(1)-O(1BL)	74.8(6)	O(1BL)-Hf(1)-O(3BL)	115.7(6)
O(2AL)-Hf(1)-O(2BL)	81.5(6)	O(1BL)-Hf(1)-O(4BL)	73.9(6)
O(2AL)-Hf(1)-O(3BL)	147.1(6)	O(2BL)-Hf(1)-O(3BL)	73.4(6)
O(2AL)-Hf(1)-O(4BL)	137.6(6)	O(2BL)-Hf(1)-O(4BL)	114.7(6)
O(3AL)-Hf(1)-O(4AL)	74.5(7)	O(3BL)-Hf(1)-O(4BL)	73.7(6)
O(1CL)-Hf(2)-O(2CL)	72.6(6)	O(3CL)-Hf(2)-O(1DL)	80.2(6)
O(1CL)-Hf(2)-O(3CL)	115.8(6)	O(3CL)-Hf(2)-O(2DL)	145.3(6)
O(1CL)-Hf(2)-O(4CL)	75.4(6)	O(3CL)-Hf(2)-O(3DL)	137.8(6)
O(1CL)-Hf(2)-O(1DL)	136.4(6)	O(3CL)-Hf(2)-O(4DL)	75.0(6)
O(1CL)-Hf(2)-O(2DL)	74.8(6)	O(4CL)-Hf(2)-O(1DL)	146.1(6)
O(1CL)-Hf(2)-O(3DL)	79.5(5)	O(4CL)-Hf(2)-O(2DL)	140.1(6)
O(1CL)-Hf(2)-O(4DL)	147.7(6)	O(4CL)-Hf(2)-O(3DL)	74.0(6)
O(2CL)-Hf(2)-O(3CL)	73.3(6)	O(4CL)-Hf(2)-O(4DL)	79.8(6)
O(2CL)-Hf(2)-O(4CL)	115.5(6)	O(1DL)-Hf(2)-O(2DL)	71.8(6)
O(2CL)-Hf(2)-O(1DL)	74.4(6)	O(1DL)-Hf(2)-O(3DL)	116.9(6)
O(2CL)-Hf(2)-O(2DL)	79.5(6)	O(1DL)-Hf(2)-O(4DL)	73.6(6)
O(2CL)-Hf(2)-O(3DL)	146.2(5)	O(2DL)-Hf(2)-O(3DL)	75.0(6)
O(2CL)-Hf(2)-O(4DL)	138.0(6)	O(2DL)-Hf(2)-O(4DL)	114.7(6)
O(3CL)-Hf(2)-O(4CL)	72.8(6)	O(3DL)-Hf(2)-O(4DL)	74.0(6)

Table S13. The differences between the neighboring O-M-O angles for **K-1** and **K-2**.

K-1		K-2	
$ \angle\text{O}(2\text{L})\text{ZrO}(2\text{LA}) - \angle\text{O}(1\text{L})\text{ZrO}(2\text{LA}) $	1.6°	$ \angle\text{O}(2\text{L})\text{HfO}(2\text{LA}) - \angle\text{O}(1\text{L})\text{HfO}(2\text{LA}) $	0.3°
$ \angle\text{O}(1\text{L})\text{ZrO}(2\text{LA}) - \angle\text{O}(1\text{L})\text{ZrO}(3\text{LA}) $	6.1°	$ \angle\text{O}(1\text{L})\text{HfO}(2\text{LA}) - \angle\text{O}(1\text{L})\text{HfO}(3\text{LA}) $	5.3°
$ \angle\text{O}(1\text{L})\text{ZrO}(3\text{LA}) - \angle\text{O}(4\text{L})\text{ZrO}(3\text{LA}) $	4.9°	$ \angle\text{O}(1\text{L})\text{HfO}(3\text{LA}) - \angle\text{O}(4\text{L})\text{HfO}(3\text{LA}) $	4.6°
$ \angle\text{O}(4\text{L})\text{ZrO}(3\text{LA}) - \angle\text{O}(4\text{L})\text{ZrO}(4\text{LA}) $	2.9°	$ \angle\text{O}(4\text{L})\text{HfO}(3\text{LA}) - \angle\text{O}(4\text{L})\text{HfO}(4\text{LA}) $	1.2°
$ \angle\text{O}(4\text{L})\text{ZrO}(4\text{LA}) - \angle\text{O}(3\text{L})\text{ZrO}(4\text{LA}) $	2.9°	$ \angle\text{O}(4\text{L})\text{HfO}(4\text{LA}) - \angle\text{O}(3\text{L})\text{HfO}(4\text{LA}) $	1.2°
$ \angle\text{O}(3\text{L})\text{ZrO}(4\text{LA}) - \angle\text{O}(3\text{L})\text{ZrO}(1\text{LA}) $	4.9°	$ \angle\text{O}(3\text{L})\text{HfO}(4\text{LA}) - \angle\text{O}(3\text{L})\text{HfO}(1\text{LA}) $	4.6°
$ \angle\text{O}(3\text{L})\text{ZrO}(1\text{LA}) - \angle\text{O}(2\text{L})\text{ZrO}(1\text{LA}) $	6.1°	$ \angle\text{O}(3\text{L})\text{HfO}(1\text{LA}) - \angle\text{O}(2\text{L})\text{HfO}(1\text{LA}) $	5.3°
$ \angle\text{O}(2\text{L})\text{ZrO}(1\text{LA}) - \angle\text{O}(2\text{L})\text{ZrO}(2\text{LA}) $	1.6°	$ \angle\text{O}(2\text{L})\text{ZrO}(1\text{LA}) - \angle\text{O}(2\text{L})\text{ZrO}(2\text{LA}) $	0.3°

Table S14. The differences between the neighboring O-M-O angles for **Et₂NH₂-3** and **Et₂NH₂-4**.

Et₂NH₂-3		Et₂NH₂-4	
∠O(4AL)Zr(1)O(4BL) – ∠O(3AL)Zr(1)O(4BL)	5.1°	∠O(4AL)Hf(1)O(4BL) – ∠O(3AL)Hf(1)O(4BL)	6.3°
∠O(3AL)Zr(1)O(4BL) – ∠O(3AL)Zr(1)O(1BL)	5.2°	∠O(3AL)Hf(1)O(4BL) – ∠O(3AL)Hf(1)O(1BL)	6.9°
∠O(3AL)Zr(1)O(1BL) – ∠O(2AL)Zr(1)O(1BL)	6.6°	∠O(3AL)Hf(1)O(1BL) – ∠O(2AL)Hf(1)O(1BL)	6.1°
∠O(2AL)Zr(1)O(1BL) – ∠O(2AL)Zr(1)O(2BL)	7.0°	∠O(2AL)Hf(1)O(1BL) – ∠O(2AL)Hf(1)O(2BL)	6.7°
∠O(2AL)Zr(1)O(2BL) – ∠O(1AL)Zr(1)O(2BL)	6.3°	∠O(2AL)Hf(1)O(2BL) – ∠O(1AL)Hf(1)O(2BL)	7.7°
∠O(1AL)Zr(1)O(2BL) – ∠O(1AL)Zr(1)O(3BL)	7.7°	∠O(1AL)Hf(1)O(2BL) – ∠O(1AL)Hf(1)O(3BL)	7.3°
∠O(1AL)Zr(1)O(3BL) – ∠O(4AL)Zr(1)O(3BL)	9.6°	∠O(1AL)Hf(1)O(3BL) – ∠O(4AL)Hf(1)O(3BL)	8.2°
∠O(4AL)Zr(1)O(3BL) – ∠O(4AL)Zr(1)O(4BL)	7.7°	∠O(4AL)Hf(1)O(3BL) – ∠O(4AL)Hf(1)O(4BL)	7.4°
∠O(4C'L)Zr(2)O(4D'L) – ∠O(3C'L)Zr(2)O(4D'L)	6.9°	∠O(4CL)Hf(2)O(4DL) – ∠O(3CL)Hf(2)O(4DL)	4.8°
∠O(3C'L)Zr(2)O(4D'L) – ∠O(3C'L)Zr(2)O(1D'L)	5.6°	∠O(3CL)Hf(2)O(4DL) – ∠O(3CL)Hf(2)O(1DL)	5.2°
∠O(3C'L)Zr(2)O(1D'L) – ∠O(2C'L)Zr(2)O(1D'L)	5.4°	∠O(3CL)Hf(2)O(1DL) – ∠O(2CL)Hf(2)O(1DL)	5.8°
∠O(2C'L)Zr(2)O(1D'L) – ∠O(2C'L)Zr(2)O(2D'L)	6.7°	∠O(2CL)Hf(2)O(1DL) – ∠O(2CL)Hf(2)O(2DL)	5.1°
∠O(2C'L)Zr(2)O(2D'L) – ∠O(1C'L)Zr(2)O(2D'L)	5.9°	∠O(2CL)Hf(2)O(2DL) – ∠O(1CL)Hf(2)O(2DL)	4.7°
∠O(1C'L)Zr(2)O(2D'L) – ∠O(1C'L)Zr(2)O(3D'L)	4.8°	∠O(1CL)Hf(2)O(2DL) – ∠O(1CL)Hf(2)O(3DL)	4.7°
∠O(1C'L)Zr(2)O(3D'L) – ∠O(4C'L)Zr(2)O(3D'L)	5.5°	∠O(1CL)Hf(2)O(3DL) – ∠O(4CL)Hf(2)O(3DL)	5.5°
∠O(4C'L)Zr(2)O(3D'L) – ∠O(4C'L)Zr(2)O(4D'L)	6.6°	∠O(4CL)Hf(2)O(3DL) – ∠O(4CL)Hf(2)O(4DL)	5.8°

Fig. S1

Fig. S2