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Sandwich-type Hf^{IV} and Zr^{IV} complexes composed of tri-lacunary Keggin polyoxometalates: structure of $[M_3(\mu\text{-}OH)_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{9-}$ (M = Hf and Zr)

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Experimental section S1. Crystallization of the crude product of **Et_2NH_2-1** obtained without refluxing, and X-ray crystallography of a 7 : 3 mixture of the α,α- and α,β-type sandwich-structure POMs.

The white powder (0.17 g) of the crude product of diethylammonium salt (**Et_2NH_2-1**) (see Experimental section in the text) was dissolved in 3.5 mL of water on a water bath at 50-60˚C. The colorless, clear solution was slowly concentrated at room temperature. After a few days, colorless prism crystals were deposited. The colorless prism crystal (0.30 × 0.08 × 0.03 mm^3) was surrounded by liquid paraffin (Paratone-N) to prevent its degradation. X-ray diffraction measurement was done by a Bruker SMART APEX CCD diffractometer at 90 K in the range of $0.88^o < \theta < 28.31^o$. The intensity data were automatically collected for Lorentz and polarization effects during integration. The structure was solved by direct methods (program SHELXS-97)[R1a] followed by subsequent difference Fourier calculation and refined by full-matrix, least-square procedure on F^2 (program SHELXL-97).[R1b] Absorption correction was performed with SADABS (empirical absorption correction).[R1c]

One of the two "W_3O_6 cap" moieties in the two tri-lacunary Keggin units was disordered. The structure was solved using a disorder model (Fig. S1). The site occupancy factors of the tungsten and oxygen atoms in the disordered cap site were

fixed at 0.71 for the tungsten and oxygen atoms labeled with A, which corresponded to the α-Keggin unit, and 0.29 for those labeled with B, which corresponded to the β-Keggin unit. Crystal data for $C_{28}H_{97}N_7O_{75}P_2W_{18}Hf_3$: M = 5638.50, monoclinic, space group $P2_1/n$, a = 27.805(4), b = 13.734(2), c = 29.936(5) Å, β = 106.264(3) °, V = 10974(3) Å^3, Z = 4, D_c = 3.413 Mg m^{-3}, μ(Mo-Kα) = 21.723 mm^{-1}. $R1$ = 0.0960, $wR2$ = 0.1719 (for all data). R_{int} = 0.0742, $R1$ = 0.0647, $wR2$ = 0.1533, GOF = 1.071 (77399 total reflections, 27199 unique reflections where $I > 2\sigma(I)$).

References

R1 (a) G. M. Sheldrick, *Acta Crystallogr., Sect A*, 1990, **46**, 467; (b) G. M. Sheldrick, SHELXL-97 program for crystal structure refinement, University of Gottingen, Germany, 1997; (c) G. M. Sheldrick, SADABS, University of Gottingen, Germany, 1996.

Experimental section S2. Crystallization of the crude product of **Et_2NH_2-2** obtained without refluxing, and X-ray crystallography of a 7 : 3 mixture of the α,α- and α,β-type sandwich-structure POMs.

The white powder (0.5 g) of the crude product of diethylammonium salt

(**Et_2NH_2-2**) (see Experimental section in the text) was dissolved in 5 mL of water on a water bath at 50-60˚C. The colorless, clear solution was slowly concentrated at room temperature. After a few days, colorless needle crystals were deposited. The colorless needle crystal (0.23 × 0.08 × 0.03 mm^3) was surrounded by liquid paraffin (Paratone-N) to prevent its degradation. X-ray diffraction measurement was done by a Bruker SMART APEX CCD diffractometer at 90 K in the range of $0.88^o < \theta < 28.35^o$.

One of the two "W_3O_6 cap" moieties in the two tri-lacunary Keggin units was disordered. The structure was solved using a disorder model (Fig. S2). The site occupancy factors of the tungsten and oxygen atoms in the disordered "W_3O_6 cap" were fixed at 0.78 for those labeled with A (α-Keggin unit) and 0.22 for those labeled with B (β-Keggin unit). Crystal data for $C_{28}H_{105}N_7O_{80}P_2W_{18}Zr_3$: M = 5465.09, monoclinic, space group $P2_1/n$, a = 27.828(3), b = 13.6970(12), c = 30.008(3) Å, β = 106.533(2) ^{o}, V = 10965.1(17) $Å^3$, Z = 4, D_c = 3.310 Mg m^{-3}, μ(Mo-Kα) = 19.194 mm^{-1}. $R1$ = 0.1043, $wR2$ = 0.1909 (for all data). R_{int} = 0.0843, $R1$ = 0.0694, $wR2$ = 0.1681, GOF = 1.110 (107125 total reflections, 27284 unique reflections where $I > 2\sigma(I)$).

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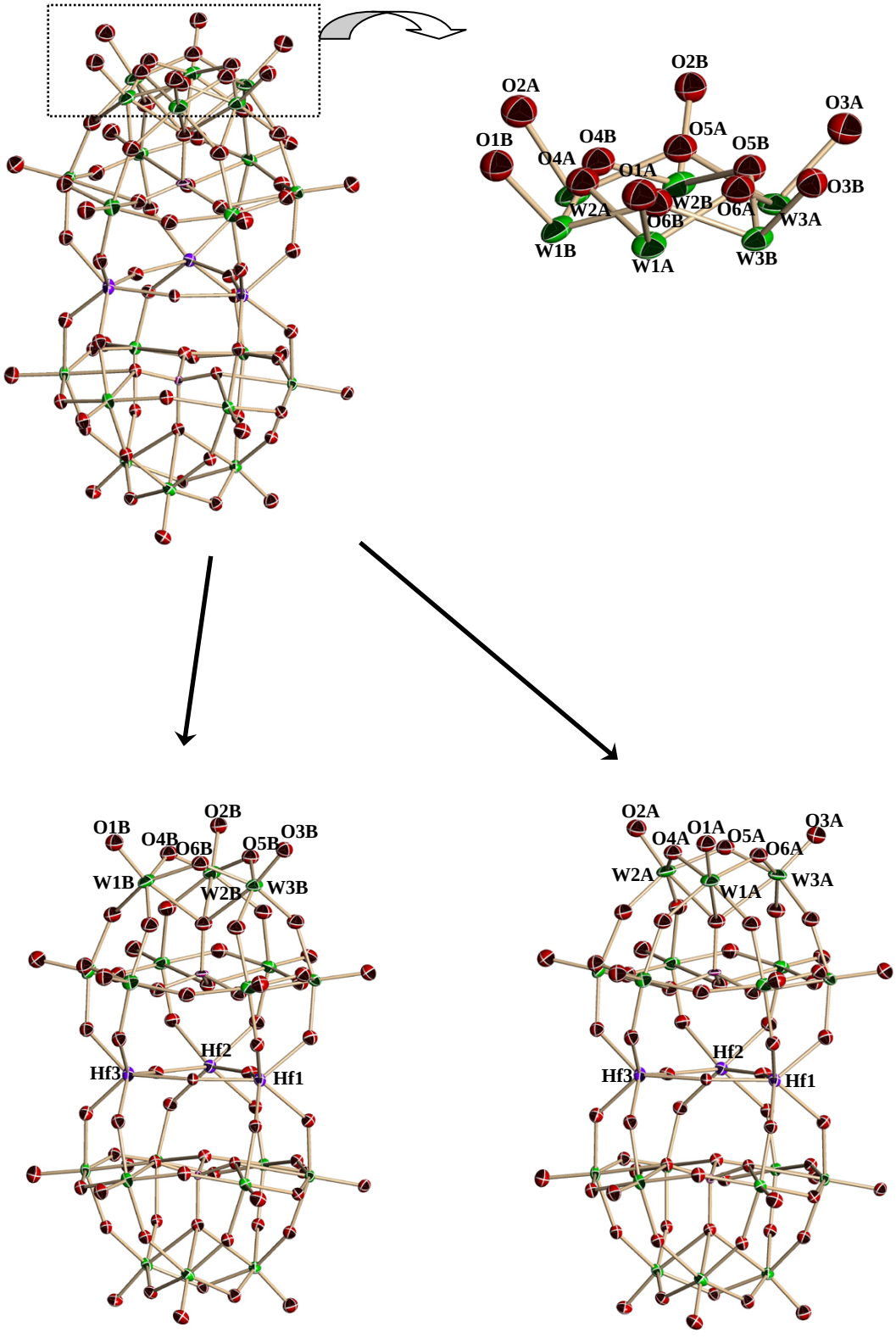

Fig. S1

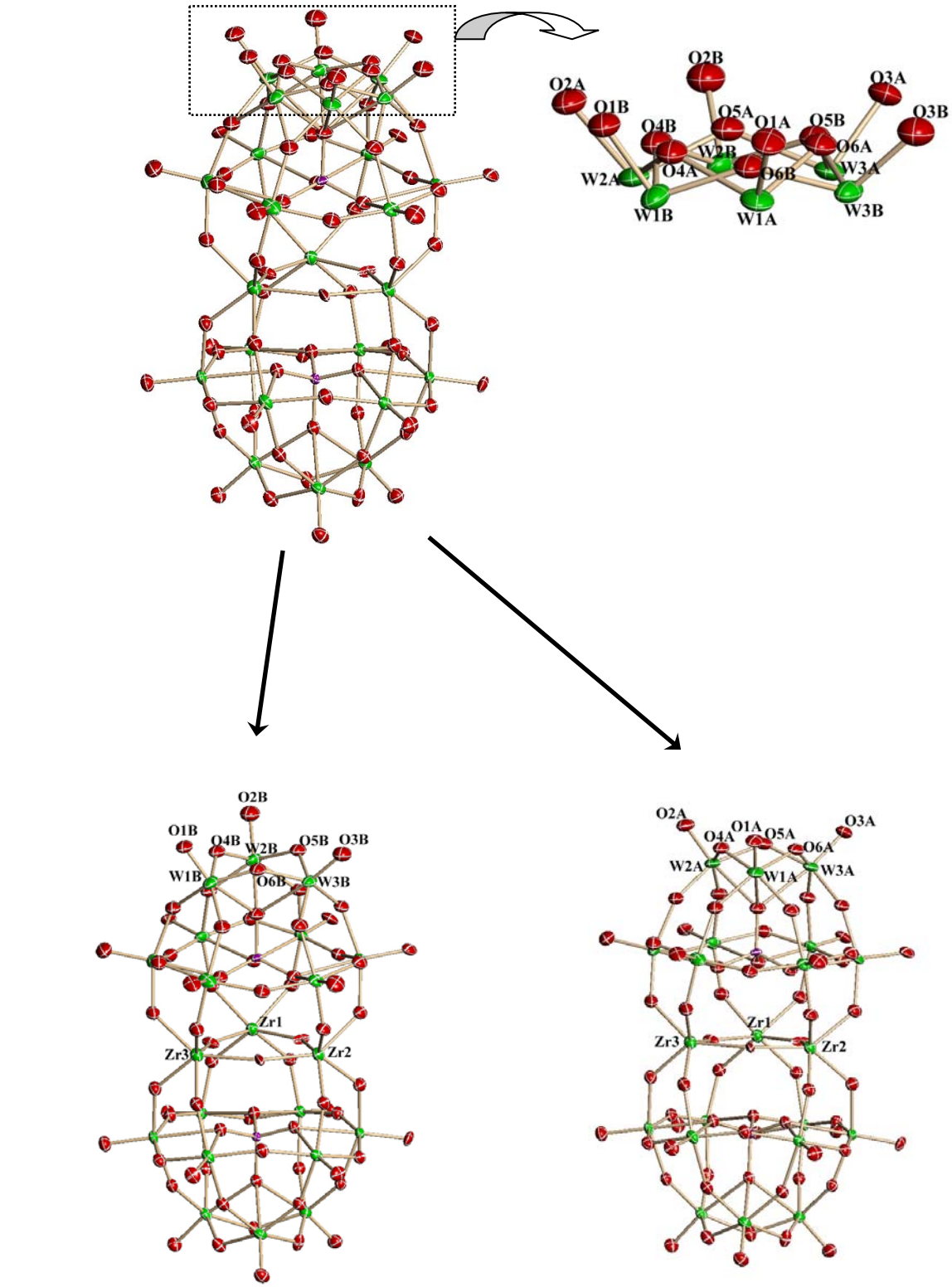

Fig. S2

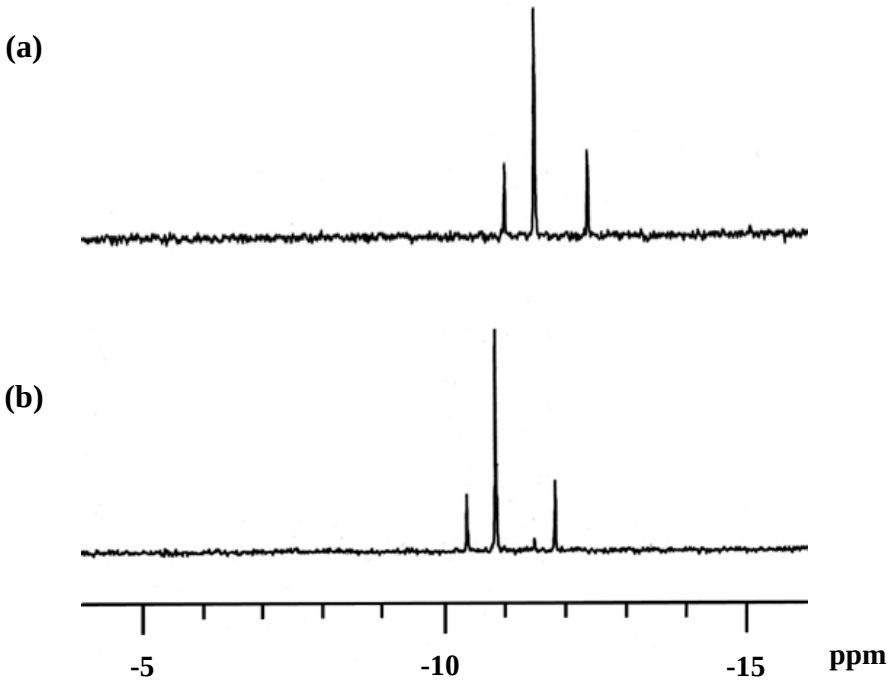

Fig. S3

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

W-O_t (O_t : terminal oxygen)			
W(1)-O(1)	1.700(7)	W(6)-O(15)	1.723(7)
W(2)-O(2)	1.699(7)	W(7)-O(16)	1.717(7)
W(3)-O(3)	1.715(7)	W(8)-O(17)	1.702(7)
W(4)-O(13)	1.709(6)	W(9)-O(18)	1.717(7)
W(5)-O(14)	1.715(6)		
		average = 1.711 [1.699(7)-1.723(7)]	
W-O_c (O_c : corner-sharing oxygen)			
W(1)-O(7)	1.897(7)	W(6)-O(27)	1.840(6)
W(1)-O(12)	1.859(7)	W(6)-O(20)	1.912(7)
W(2)-O(8)	1.872(7)	W(6)-O(9)	1.949(6)
W(2)-O(9)	1.882(7)	W(7)-O(28)	1.834(6)
W(3)-O(10)	1.869(7)	W(7)-O(22)	1.917(7)
W(3)-O(11)	1.876(7)	W(7)-O(10)	1.952(7)
W(4)-O(25)	1.851(7)	W(8)-O(29)	1.823(6)
W(4)-O(24)	1.919(6)	W(8)-O(22)	1.912(7)
W(4)-O(7)	1.931(7)	W(8)-O(11)	1.955(7)
W(5)-O(26)	1.833(6)	W(9)-O(30)	1.822(7)
W(5)-O(20)	1.903(6)	W(9)-O(24)	1.905(6)
W(5)-O(8)	1.955(7)	W(9)-O(12)	1.969(7)
		average = 1.893 [1.822(7)-1.969(7)]	
W-O_e (O_e : edge-sharing oxygen)			
W(1)-O(4)	1.959(7)	W(4)-O(19)	1.925(6)
W(1)-O(6)	1.932(7)	W(5)-O(19)	1.938(6)
W(2)-O(5)	1.933(7)	W(6)-O(21)	1.901(7)
W(2)-O(4)	1.939(7)	W(7)-O(21)	1.924(7)
W(3)-O(6)	1.941(7)	W(8)-O(23)	1.944(6)
W(3)-O(5)	1.927(7)	W(9)-O(23)	1.956(6)
		average = 1.935 [1.901(7)-1.959(7)]	
W-O_a (oxygen coordinating to P atom)			
W(1)-O(34)	2.425(6)	W(6)-O(32)	2.434(6)
W(2)-O(34)	2.424(6)	W(7)-O(32)	2.393(6)
W(3)-O(34)	2.420(6)	W(8)-O(33)	2.396(6)
W(4)-O(31)	2.418(6)	W(9)-O(33)	2.422(6)

Table S1 continued

W(5)-O(31)	2.420(6)	average = 2.417 [2.393(6)-2.434(6)]	
P-O			
P(1)-(31)	1.540(6)	P(1)-(33)	1.533(6)
P(1)-(32)	1.535(6)	P(1)-(34)	1.559(7)
		average = 1.542 [1.533(6)-1.559(7)]	
O-P-O			
O(33)-P(1)-O(32)	110.4(4)	O(33)-P(1)-O(34)	108.4(4)
O(33)-P(1)-O(31)	110.5(4)	O(32)-P(1)-O(34)	108.7(4)
O(32)-P(1)-O(31)	110.6(3)	O(31)-P(1)-O(34)	108.2(4)
		average = 109.5 [108.2(4)-110.6(3)]	

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

W-O_t (O_t : terminal oxygen)			
W(1)-O(1)	1.716(5)	W(6)-O(15)	1.717(5)
W(2)-O(2)	1.707(6)	W(7)-O(16)	1.716(5)
W(3)-O(3)	1.722(5)	W(8)-O(17)	1.718(6)
W(4)-O(13)	1.712(5)	W(9)-O(18)	1.713(5)
W(5)-O(14)	1.720(5)		
		average = 1.716 [1.707(6)-1.722(5)]	
W-O_c (O_c : corner-sharing oxygen)			
W(1)-O(7)	1.878(6)	W(6)-O(27)	1.839(5)
W(1)-O(12)	1.867(5)	W(6)-O(20)	1.925(5)
W(2)-O(8)	1.852(5)	W(6)-O(9)	1.935(5)
W(2)-O(9)	1.886(5)	W(7)-O(28)	1.829(5)
W(3)-O(10)	1.875(6)	W(7)-O(22)	1.891(5)
W(3)-O(11)	1.884(5)	W(7)-O(10)	1.952(5)
W(4)-O(25)	1.828(5)	W(8)-O(29)	1.849(5)
W(4)-O(24)	1.916(5)	W(8)-O(22)	1.924(5)
W(4)-O(7)	1.954(6)	W(8)-O(11)	1.945(5)
W(5)-O(26)	1.826(5)	W(9)-O(30)	1.833(5)
W(5)-O(20)	1.896(5)	W(9)-O(24)	1.912(5)
W(5)-O(8)	1.971(5)	W(9)-O(12)	1.954(5)
		average = 1.893 [1.826(5)-1.971(5)]	
W-O_e (O_e : edge-sharing oxygen)			
W(1)-O(4)	1.943(6)	W(4)-O(19)	1.934(5)
W(1)-O(6)	1.920(6)	W(5)-O(19)	1.951(5)
W(2)-O(5)	1.963(6)	W(6)-O(21)	1.927(5)
W(2)-O(4)	1.926(6)	W(7)-O(21)	1.932(5)
W(3)-O(6)	1.932(6)	W(8)-O(23)	1.911(6)
W(3)-O(5)	1.934(5)	W(9)-O(23)	1.911(6)
		average = 1.932 [1.911(6)-1.963(6)]	
W-O_a (oxygen coordinating to P atom)			
W(1)-O(34)	2.425(5)	W(6)-O(32)	2.419(5)
W(2)-O(34)	2.415(5)	W(7)-O(32)	2.429(5)
W(3)-O(34)	2.433(5)	W(8)-O(33)	2.435(5)
W(4)-O(31)	2.401(5)	W(9)-O(33)	2.395(5)

Table S2 continued

W(5)-O(31)	2.428(5)	average = 2.420 [2.395(5)-2.435(5)]	
P-O			
P(1)-O(31)	1.528(5)	P(1)-O(33)	1.538(5)
P(1)-O(32)	1.532(5)	P(1)-O(34)	1.561(5)
		average = 1.540 [1.528(5)-1.561(5)]	
O-P-O			
O(33)-P(1)-O(32)	110.8(3)	O(33)-P(1)-O(34)	109.0(3)
O(33)-P(1)-O(31)	110.1(3)	O(32)-P(1)-O(34)	108.4(3)
O(32)-P(1)-O(31)	110.4(3)	O(31)-P(1)-O(34)	108.2(3)
		average = 109.5 [108.2(3)-110.8(3)]	

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

O(1)	1.798	O(29)	1.996	W(1)	6.129
O(2)	1.803	O(30)	1.996	W(2)	6.185
O(3)	1.726	O(31)	1.746	W(3)	6.149
O(4)	1.835	O(32)	1.772	W(4)	6.144
O(5)	1.931	O(33)	1.784	W(5)	6.124
O(6)	1.897	O(34)	1.934	W(6)	6.143
O(7)	2.018			W(7)	6.137
O(8)	2.032	O(1M)	1.220	W(8)	6.197
O(9)	2.016	O(2M)	1.222	W(9)	6.067
O(10)	2.048				
O(11)	2.020			Hf(1)	4.046
O(12)	2.039			Hf(2)	4.033
O(13)	1.754				
O(14)	1.726			P(1)	4.904
O(15)	1.689				
O(16)	1.717				
O(17)	1.788				
O(18)	1.717				
O(19)	1.923				
O(20)	2.052				
O(21)	2.025				
O(22)	2.015				
O(23)	1.830				
O(24)	2.028				
O(25)	1.912				
O(26)	1.954				
O(27)	1.918				
O(28)	1.968				

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

O(1)	1.722	O(29)	1.856	W(1)	6.155
O(2)	1.764	O(30)	1.918	W(2)	6.163
O(3)	1.694	O(31)	1.794	W(3)	6.071
O(4)	1.908	O(32)	1.766	W(4)	6.145
O(5)	1.838	O(33)	1.759	W(5)	6.068
O(6)	1.952	O(34)	1.925	W(6)	6.114
O(7)	2.016			W(7)	6.184
O(8)	2.056	O(1M)	1.141	W(8)	6.085
O(9)	2.040	O(2M)	1.136	W(9)	6.200
O(10)	2.030				
O(11)	2.020			Zr(1)	3.778
O(12)	2.050			Zr(2)	3.753
O(13)	1.740				
O(14)	1.703			P(1)	4.932
O(15)	1.717				
O(16)	1.722				
O(17)	1.712				
O(18)	1.736				
O(19)	1.867				
O(20)	2.037				
O(21)	1.934				
O(22)	2.054				
O(23)	2.033				
O(24)	2.016				
O(25)	1.930				
O(26)	1.940				
O(27)	1.891				
O(28)	1.909				