

Electronic Supplementary Information

Distorted Cubic Tetranuclear Vanadium(IV) Phosphonate Cages :

Double-Four-Ring (D4R) Containing Transition Metal ion

Phosphonate cages

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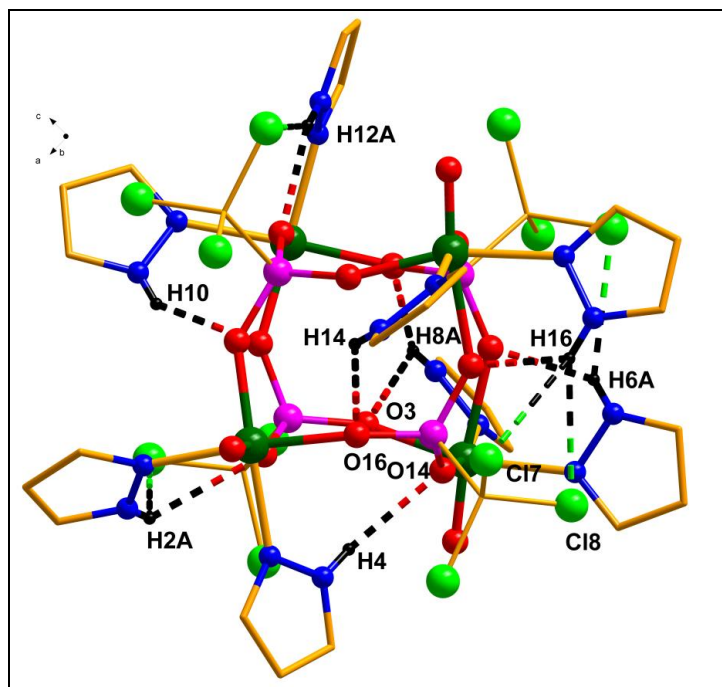


Fig. S1 Intramolecular hydrogen-bonding in 1.

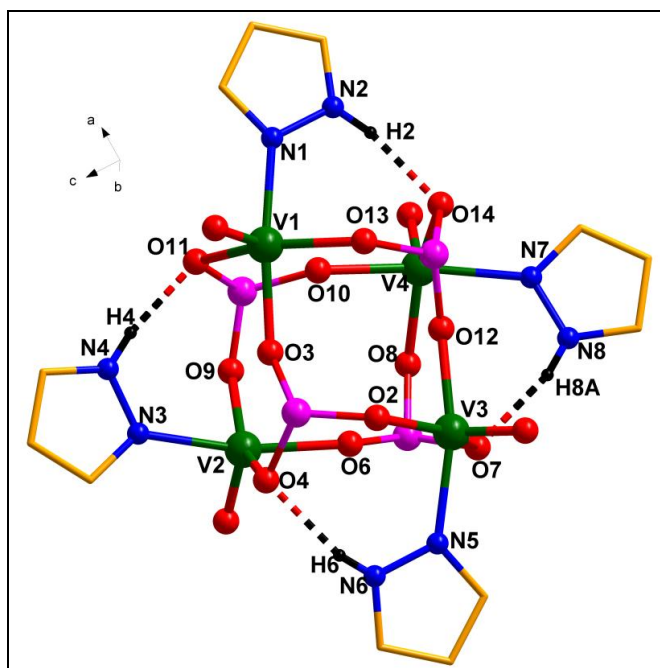


Fig. S2 Intramolecular hydrogen-bonding in 2.

Table S1 Hydrogen bond parameters of **1**.

D-H---A	d(D-H)	d(H---A)	<DHA	d(D-A)
N4-H4---- O14	0.860	2.301	144.10	3.040
N10-H10---- O4	0.860	2.189	117.65	2.698
N14-H14----O12	0.860	2.226	110.91	2.658
N14-H14----O16	0.860	2.402	139.95	3.109
N16-H16----O15	0.860	2.162	117.54	2.671
N16-H16----Cl8	0.860	2.860	145.80	3.604
N16-H16----Cl7	0.860	2.929	149.67	3.697
N2-H2A----O2	0.860	2.390	111.23	2.818
N2-H2A----Cl1	0.860	2.840	111.05	3.249
N6-H6A----O6	0.860	2.078	123.15	2.648
N6-H6A----Cl5	0.860	2.710	153.24	3.500
N8-H8A----O8	0.860	2.199	152.48	2.988
N8-H8A----O3	0.860	2.322	113.96	2.735
N12-H12A----O10	0.860	2.152	120.72	2.694
N12-H12A----Cl11	0.860	2.775	156.10	3.579

Table S2 Hydrogen bond parameters of **2**.

D-H---A	d(D-H)	d(H---A)	<DHA	d(D-A)
N2-H2----- O14	0.860	1.919	160.18	2.743
N4-H4----- O11	0.860	1.895	163.15	2.729
N6-H6----- O4	0.860	1.907	158.28	2.724
N8-H8A---- O7	0.860	1.957	160.10	2.781

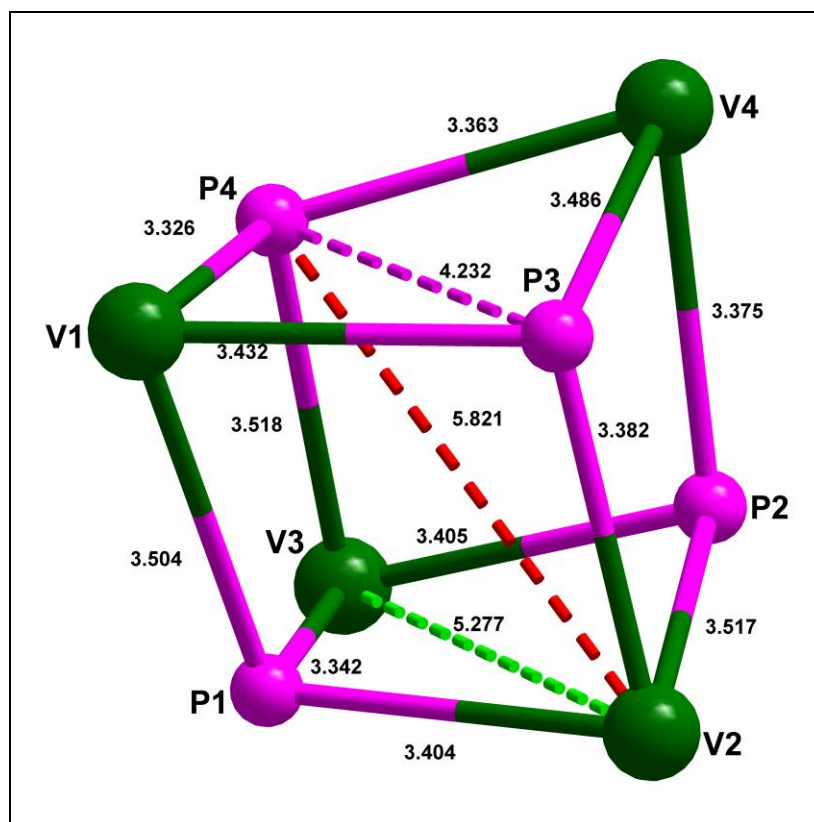


Fig. S3 Distorted cubane core of **1**. Edges and diagonal distances (\AA) are given in the figure. Bond angles (deg): V1-P1-V2 100.202(25); V1-P1-V3 106.854(25); V2-P2-V4 105.144(28); V2-P2-V3 99.328(27); V1-P3-V2 102.105(26); V1-P3-V4 98.343(28); V4-P4-V1 102.989(29); V4-P4-V3 99.515(26); P1-V1-P4 72.639(22); P1-V1-P3 75.419(22); P1-V2-P2 75.258(25); P1-V2-P3 77.406(24); P2-V4-P4 78.318(24); P2-V4-P3 74.379(24); P4-V3-P2 75.835(24); P4-V3-P1 72.274(23).

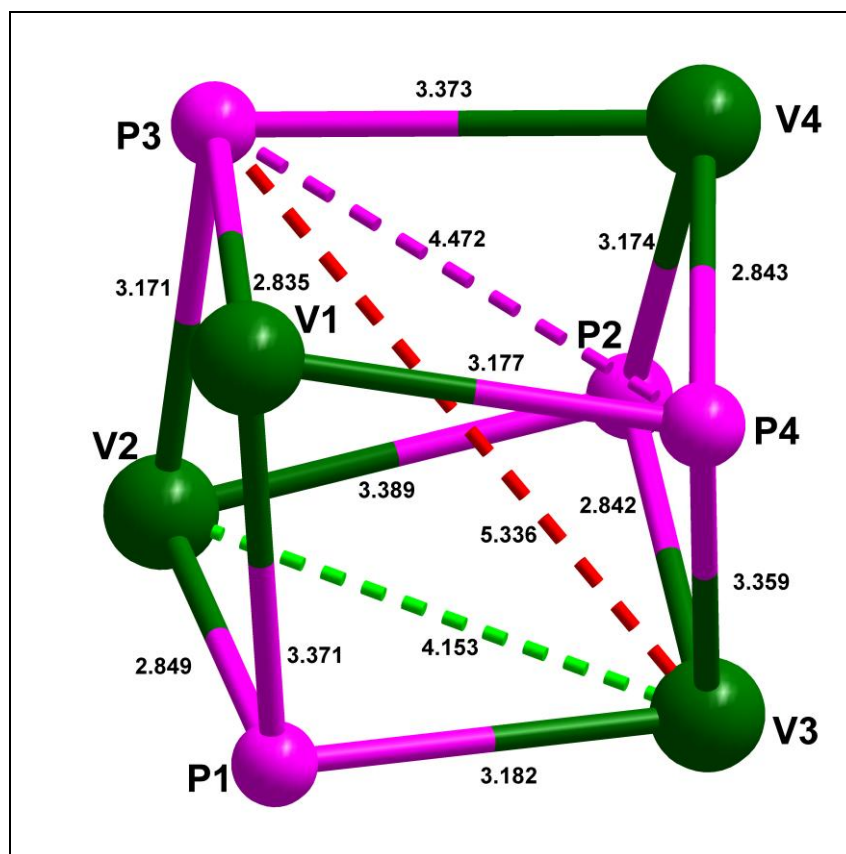


Fig. S4 Distorted cubane core of **2**. Edges and diagonal distances (\AA) are given in the figure.

Bond angles (deg): V2-P1-V3 86.866(28); V2-P1-V1 83.719(27); V4-P2-V3 87.293(28); V4-P2-V2 98.009(28); V2-P3-V4 98.395(28); V2-P3-V1 87.727(29); V4-P4-V3 83.782(27); V4-P4-V1 86.747(28); P3-V1-P4 95.948(29); P3-V1-P1 91.279(28); P3-V2-P1 95.255(29); P1-V2-P2 91.562(28); P1-V3-P4 77.669(26); P2-V3-P1 96.113(29); P2-V3-P4 91.524(28); P4-V4-P3 91.616(28); P4-V4-P2 95.451(29); P3-V4-P2 78.310(26).

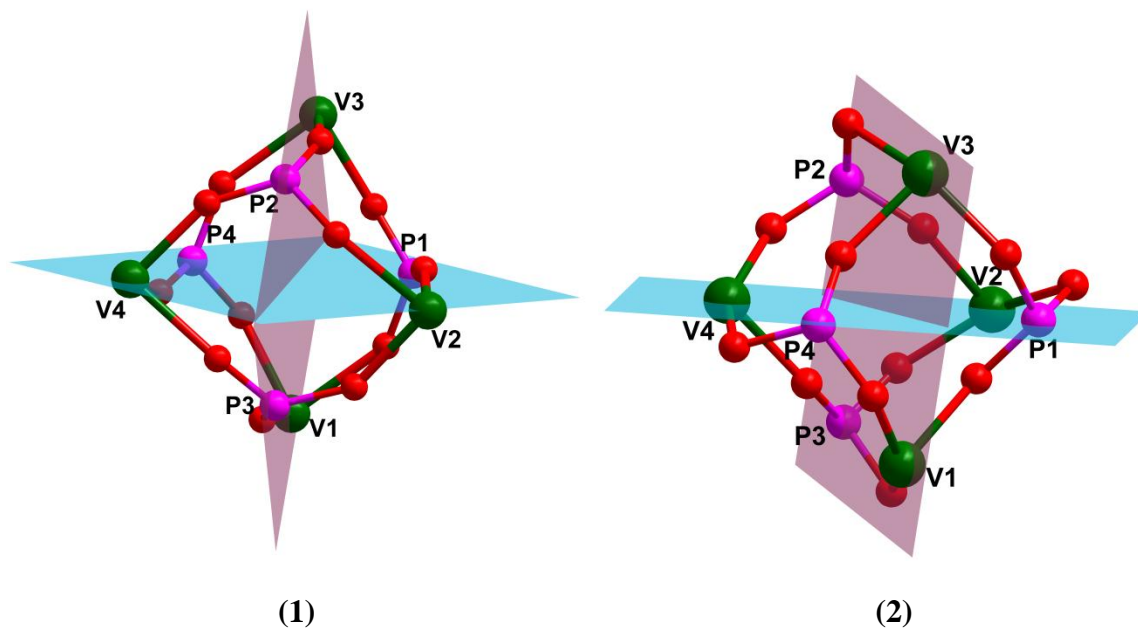


Fig. S5 Representation of the two dinuclear segments of complexes **1** and **2**. The angle between two V_2P_2 plane is $89.374(11)^\circ$ (**1**) and $89.855(11)^\circ$ (**2**).

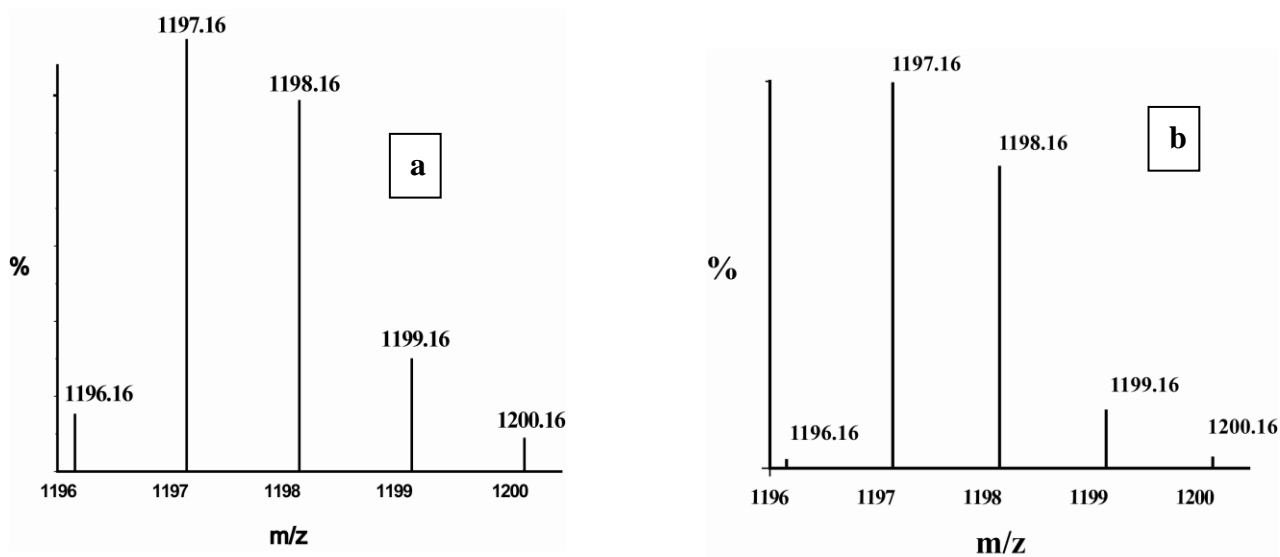


Fig. S6 (a) ESI-MS spectrum of complex **2**, (b) simulated isotopic pattern.

Table S3. Bond Lengths [Å] and Angles [deg] for **1**.

Bond Lengths/Å or Bond Angles/deg							
N(1)-V(1)	2.126(3)	N(5)-V(2)	2.141(3)	N(9)-V(3)	2.148(3)	N(13)-V(4)	2.143(3)
N(3)-V(1)	2.132(3)	N(7)-V(2)	2.140(3)	N(11)-V(3)	2.113(3)	N(15)-V(4)	2.143(3)
O(1)-V(1)	1.602(2)	O(3)-V(2)	1.982(2)	O(4)-V(3)	2.005(2)	O(7)-V(4)	1.973(2)
O(2)-V(1)	2.157(2)	O(5)-V(2)	1.597(2)	O(8)-V(3)	2.014(2)	O(12)-V(4)	1.978(2)
O(11)-V(1)	2.015(2)	O(6)-V(2)	2.187(2)	O(9)-V(3)	1.594(2)	O(13)-V(4)	1.590(2)
O(16)-V(1)	2.020(2)	O(14)-V(2)	2.007(2)	O(10)-V(3)	2.168(2)	O(15)-V(4)	2.192(2)
O(2)-P(1)	1.499(2)	O(10)-P(4)	1.495(2)	N(13)-N(14)	1.359(4)	N(16)-H(16)	0.86
O(3)-P(1)	1.502(2)	O(11)-P(4)	1.516(2)	N(15)-N(16)	1.363(4)		
O(4)-P(1)	1.508(2)	O(12)-P(4)	1.507(2)	N(2)-H(2A)	0.86		
O(6)-P(2)	1.502(2)	N(1)-N(2)	1.365(4)	N(4)-H(4)	0.86		
O(7)-P(2)	1.499(2)	N(3)-N(4)	1.367(4)	N(6)-H(6A)	0.86		
O(8)-P(2)	1.514(2)	N(5)-N(6)	1.349(4)	N(8)-H(8A)	0.86		
O(14)-P(3)	1.511(2)	N(7)-N(8)	1.362(4)	N(10)-H(10)	0.86		
O(15)-P(3)	1.492(2)	N(9)-N(10)	1.344(4)	N(12)-H(12A)	0.86		
O(16)-P(3)	1.508(2)	N(11)-N(12)	1.347(4)	N(14)-H(14)	0.86		
O(1)-V(1)-O(11)	102.56(10)	O(14)-V(2)-N(7)	167.02(10)	O(9)-V(3)-O(10)	171.34(10)		
O(1)-V(1)-O(16)	94.21(11)	O(5)-V(2)-N(5)	93.33(11)	O(4)-V(3)-O(10)	83.82(9)		
O(11)-V(1)-O(16)	93.71(9)	O(3)-V(2)-N(5)	165.85(10)	O(8)-V(3)-O(10)	91.46(9)		
O(1)-V(1)-N(1)	91.73(11)	O(14)-V(2)-N(5)	88.96(10)	N(11)-V(3)-O(10)	82.39(10)		
O(11)-V(1)-N(1)	89.72(10)	N(7)-V(2)-N(5)	96.55(11)	N(9)-V(3)-O(10)	79.05(10)		
O(16)-V(1)-N(1)	172.33(10)	O(5)-V(2)-O(6)	171.24(11)	O(13)-V(4)-O(7)	98.43(12)		
O(1)-V(1)-N(3)	96.79(11)	O(3)-V(2)-O(6)	84.72(9)	O(13)-V(4)-O(12)	102.71(11)		
O(11)-V(1)-N(3)	160.51(10)	O(14)-V(2)-O(6)	88.74(9)	O(7)-V(4)-O(12)	91.12(10)		
O(16)-V(1)-N(3)	87.16(10)	N(7)-V(2)-O(6)	80.52(10)	O(13)-V(4)-N(13)	94.11(12)		
N(1)-V(1)-N(3)	87.33(11)	N(5)-V(2)-O(6)	81.34(10)	O(7)-V(4)-N(13)	166.53(11)		
O(1)-V(1)-O(2)	170.78(11)	O(9)-V(3)-O(4)	99.51(11)	O(12)-V(4)-N(13)	81.29(10)		
O(11)-V(1)-O(2)	83.34(9)	O(9)-V(3)-O(8)	96.36(10)	O(13)-V(4)-N(15)	91.90(12)		
O(16)-V(1)-O(2)	92.45(9)	O(4)-V(3)-O(8)	92.48(9)	O(7)-V(4)-N(15)	93.52(10)		
N(1)-V(1)-O(2)	81.13(10)	O(9)-V(3)-N(11)	94.21(12)	O(12)-V(4)-N(15)	163.85(10)		
N(3)-V(1)-O(2)	77.17(10)	O(4)-V(3)-N(11)	166.20(11)	N(13)-V(4)-N(15)	90.96(11)		

O(5)-V(2)-O(3) 100.80(11) O(8)-V(3)-N(11) 87.41(10) O(13)-V(4)-O(15) 170.31(11)
 O(5)-V(2)-O(14) 98.15(11) O(9)-V(3)-N(9) 93.30(11) O(7)-V(4)-O(15) 85.36(9)
 O(3)-V(2)-O(14) 88.34(9) O(4)-V(3)-N(9) 83.86(10) O(12)-V(4)-O(15) 86.06(9)
 O(5)-V(2)-N(7) 93.27(11) O(8)-V(3)-N(9) 170.13(10) N(13)-V(4)-O(15) 83.05(10)
 O(3)-V(2)-N(7) 83.46(10) N(11)-V(3)-N(9) 93.96(11) N(15)-V(4)-O(15) 78.92(10)

P(1)-O(2)-V(1) 146.21(14) P(3)-O(14)-V(2) 147.71(14)
 P(1)-O(3)-V(2) 155.01(15) P(3)-O(15)-V(4) 141.48(13)
 P(1)-O(4)-V(3) 143.71(14) P(3)-O(16)-V(1) 152.91(15)
 P(2)-O(6)-V(2) 144.17(14) P(4)-O(10)-V(3) 147.03(14)
 P(2)-O(7)-V(4) 152.64(15) P(4)-O(11)-V(1) 140.41(14)
 P(2)-O(8)-V(3) 149.32(14) P(4)-O(12)-V(4) 149.31(15)

Table S4 Bond Lengths [\AA] and Angles [deg] for **2**.

Bond Lengths/ \AA or Bond Angles/deg							
N(1)-V(1)	2.116(3)	N(3)-V(2)	2.119(3)	N(5)-V(3)	2.115(3)	N(7)-V(4)	2.116(3)
O(13)-V(1)	1.960(2)	O(4)-V(2)	2.019(2)	O(2)-V(3)	1.969(2)	O(14)-V(4)	2.019(2)
O(1)-V(1)	1.589(2)	O(5)-V(2)	1.584(2)	O(7)-V(3)	2.021(2)	O(16)-V(4)	1.581(2)
O(3)-V(1)	2.027(2)	O(6)-V(2)	2.029(2)	O(12)-V(3)	2.020(2)	O(8)-V(4)	1.961(2)
O(11)-V(1)	2.015(2)	O(9)-V(2)	1.960(2)	O(15)-V(3)	1.584(2)	O(10)-V(4)	2.028(2)
O(2)-P(1)	1.523(2)	O(11)-P(3)	1.552(2)	N(1)-N(2)	1.360(4)		
O(3)-P(1)	1.534(2)	O(9)-P(3)	1.519(2)	N(3)-N(4)	1.346(3)		
O(4)-P(1)	1.553(2)	O(10)-P(3)	1.537(2)	N(7)-N(8)	1.356(3)		
O(6)-P(2)	1.546(2)	O(13)-P(4)	1.521(2)	N(5)-N(6)	1.360(4)		
O(7)-P(2)	1.546(2)	O(14)-P(4)	1.550(2)				
O(8)-P(2)	1.522(2)	O(12)-P(4)	1.539(2)				
O(13)-V(1)-O(11)	148.73(9)	O(4)-V(2)-N(3)	85.81(10)	O(8)-V(4)-N(7)	89.67(10)		
O(13)-V(1)-O(3)	88.43(9)	O(6)-V(2)-N(3)	163.67(10)	O(14)-V(4)-N(7)	86.51(10)		

O(11)-V(1)-O(3)	85.20(9)	O(2)-V(3)-O(12)	89.03(9)	O(10)-V(4)-N(7)	165.13(10)
O(13)-V(1)-N(1)	90.36(10)	O(2)-V(3)-O(7)	148.79(9)		
O(11)-V(1)-N(1)	87.62(10)	O(12)-V(3)-O(7)	84.76(9)		
O(3)-V(1)-N(1)	164.07(10)	O(2)-V(3)-N(5)	90.16(10)		
O(5)-V(2)-O(9)	107.76(11)	O(12)-V(3)-N(5)	163.08(10)		
O(5)-V(2)-O(4)	104.41(11)	O(7)-V(3)-N(5)	87.21(10)		
O(9)-V(2)-O(4)	147.81(9)	O(8)-V(4)-O(14)	147.97(9)		
O(9)-V(2)-O(6)	89.34(9)	O(8)-V(4)-O(10)	89.64(9)		
O(4)-V(2)-O(6)	85.96(9)	O(14)-V(4)-O(10)	86.21(9)		
O(9)-V(2)-N(3)	90.15(10)				
P(1)-O(2)-V(3)	130.90(13)	P(3)-O(9)-V(2)	130.92(13)		
P(1)-O(3)-V(1)	141.91(14)	P(3)-O(10)-V(4)	141.84(14)		
P(1)-O(4)-V(2)	105.09(12)	P(3)-O(11)-V(1)	104.56(12)		
P(2)-O(6)-V(2)	142.52(14)	P(4)-O(12)-V(3)	141.03(14)		
P(2)-O(7)-V(3)	104.87(11)	P(4)-O(13)-V(1)	131.39(14)		
P(2)-O(8)-V(4)	130.87(14)	P(4)-O(14)-V(4)	104.87(12)		
