Electronic Supplementary Information (ESI)

Di-, Tri- and Tetranuclear Molecular Vanadium Phosphonates: A Chloride Encapsulated Tetranuclear Bowl

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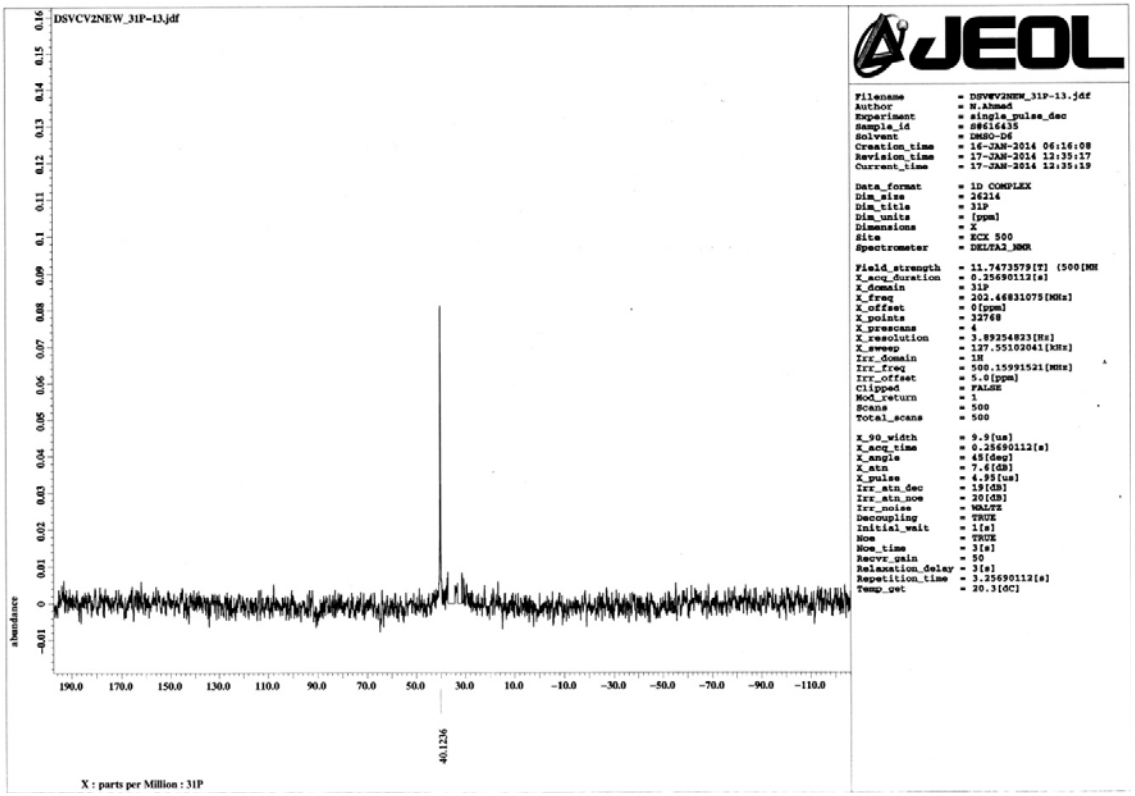


Fig. S1 ^{31}P NMR of **3**.

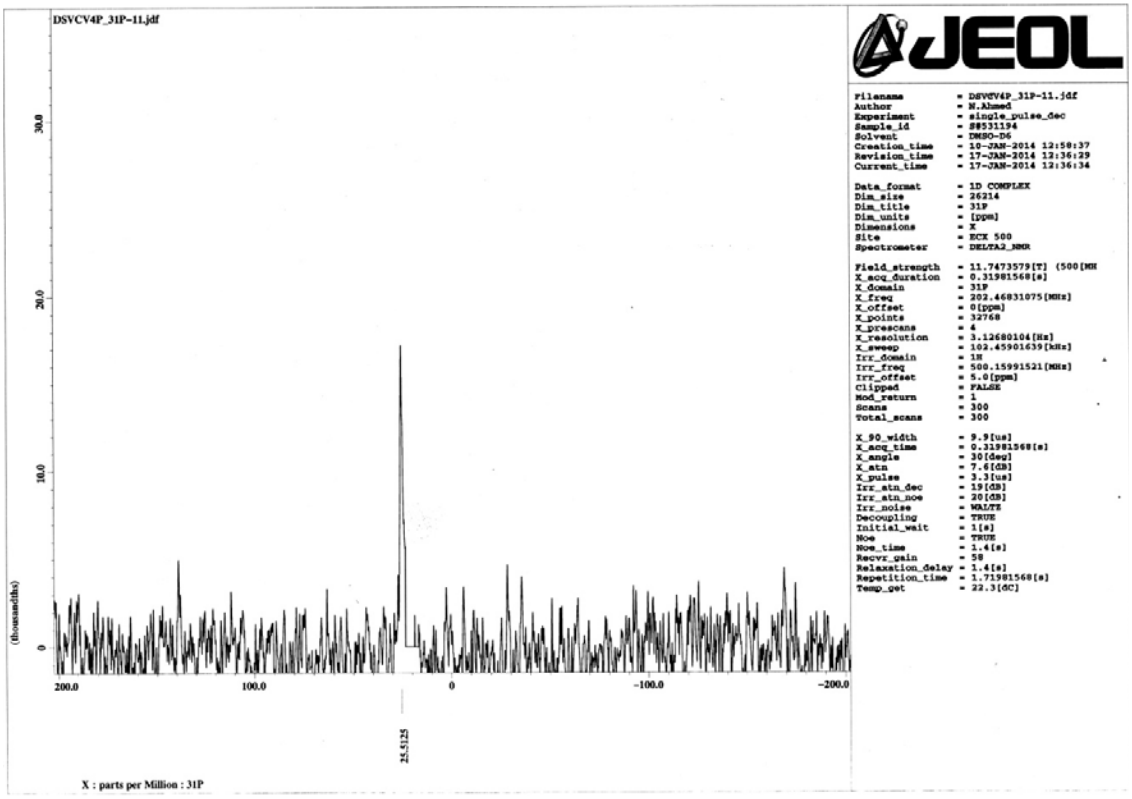


Fig. S2 ^{31}P NMR of **6**.

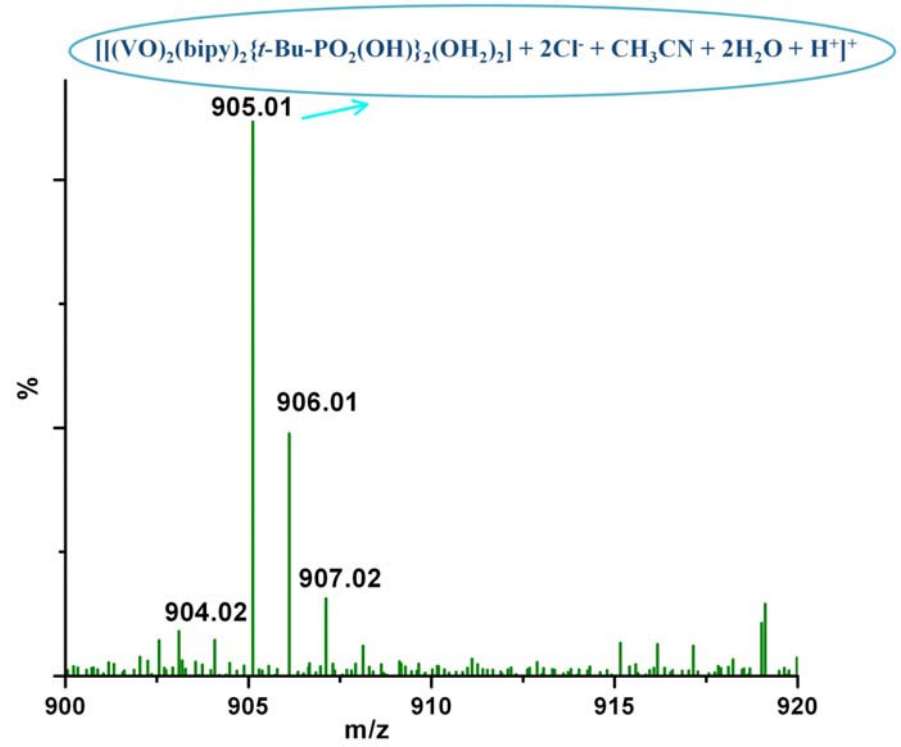


Fig. S3 ESI-MS of **2**.

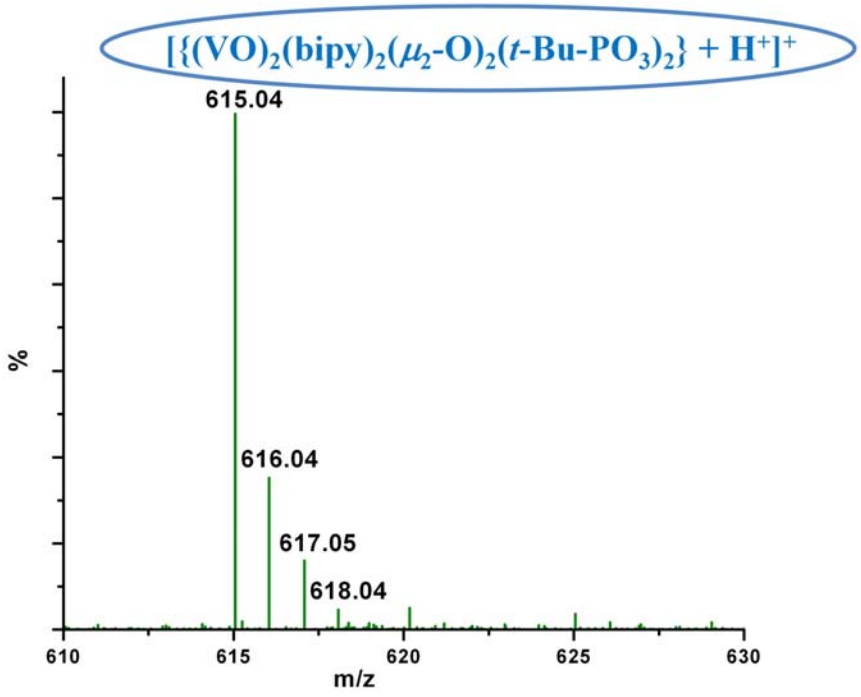


Fig. S4 ESI-MS of **3**.

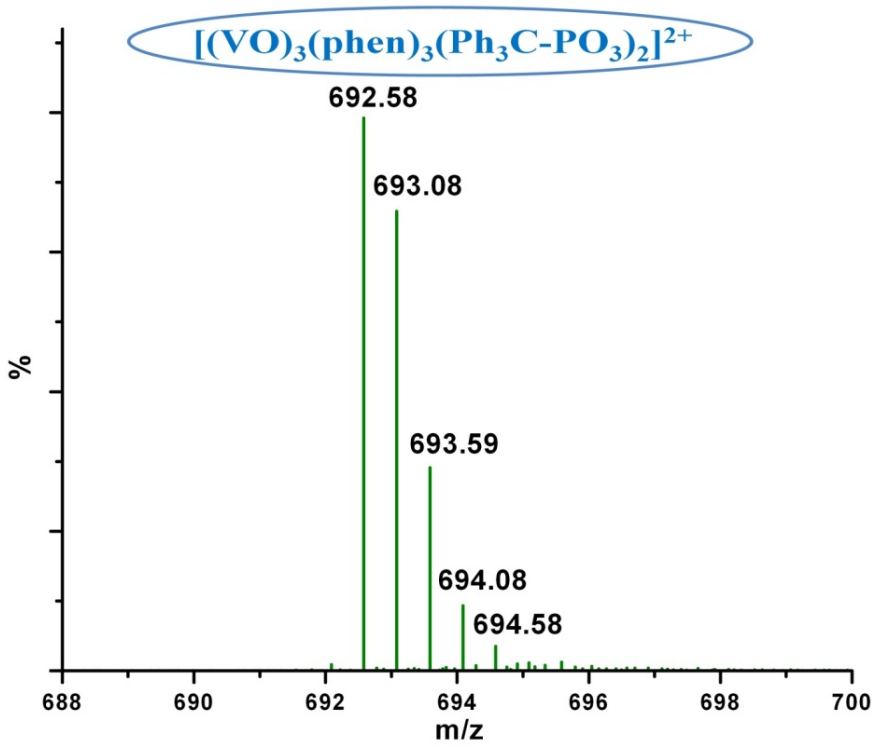


Fig. S5 ESI-MS of **4**.

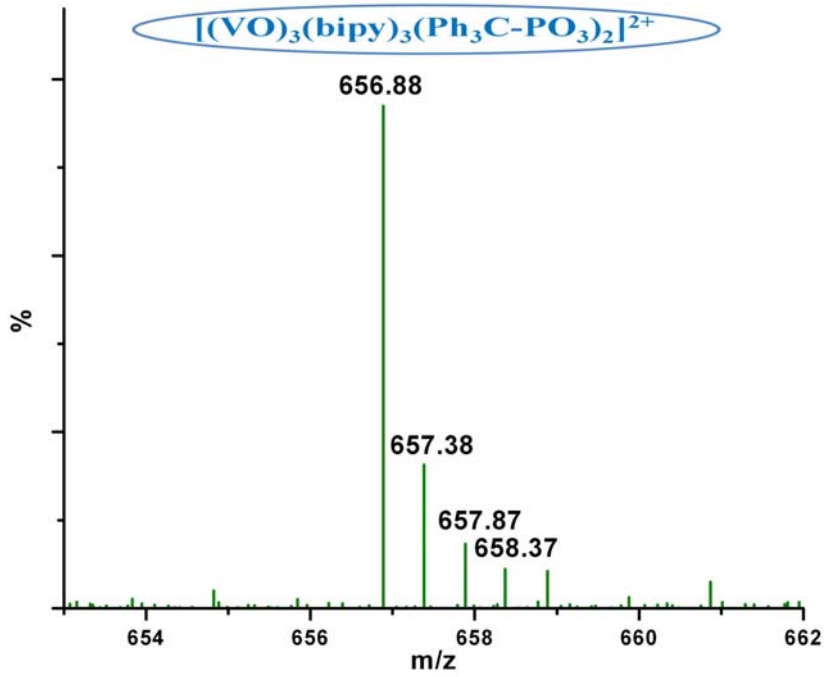


Fig. S6 ESI-MS of **5**.

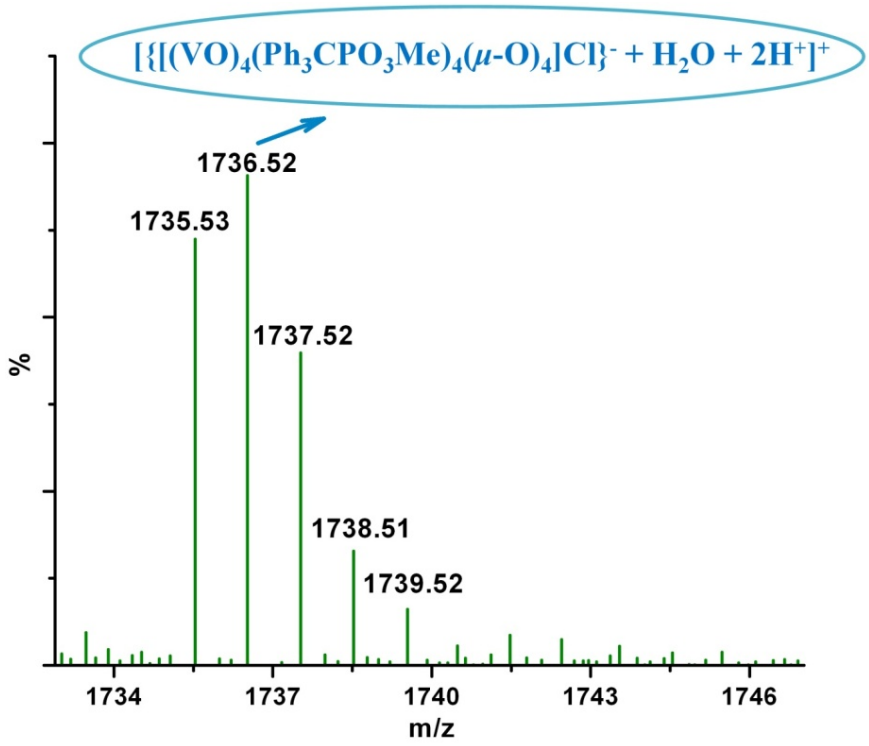


Fig. S7 ESI-MS of **6**.

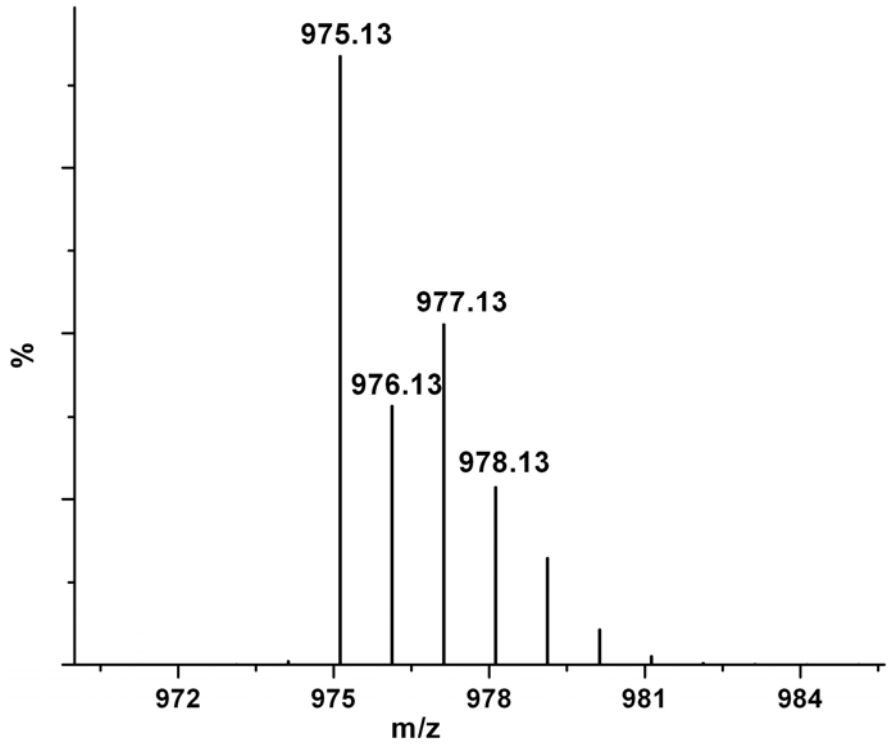


Fig. S8 Simulated ESI-MS of **1**.

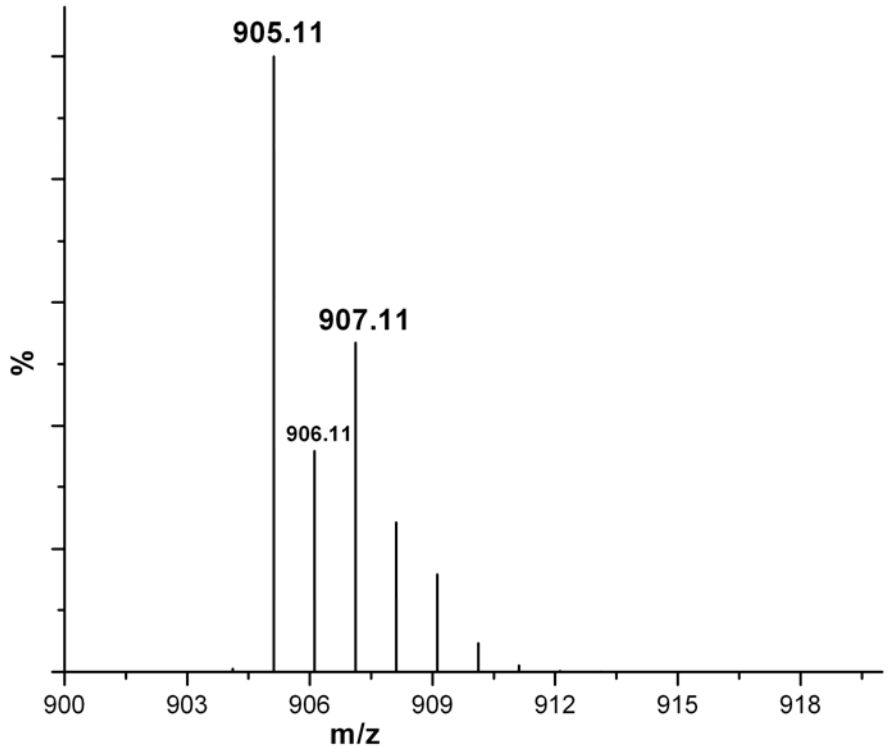


Fig. S9 Simulated ESI-MS of **2**.

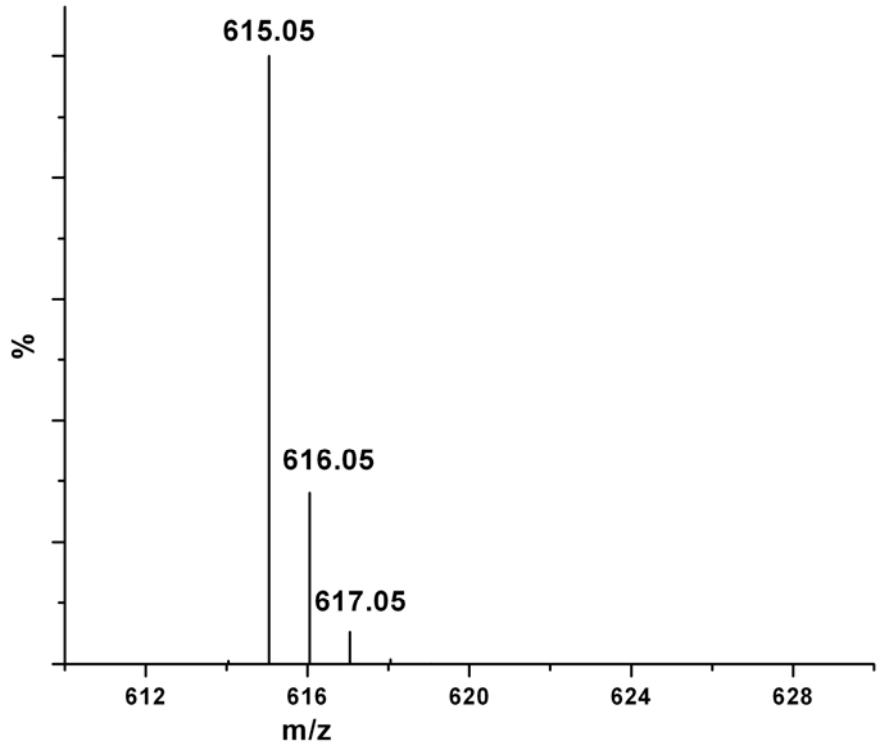


Fig. S10 Simulated ESI-MS of **3**.

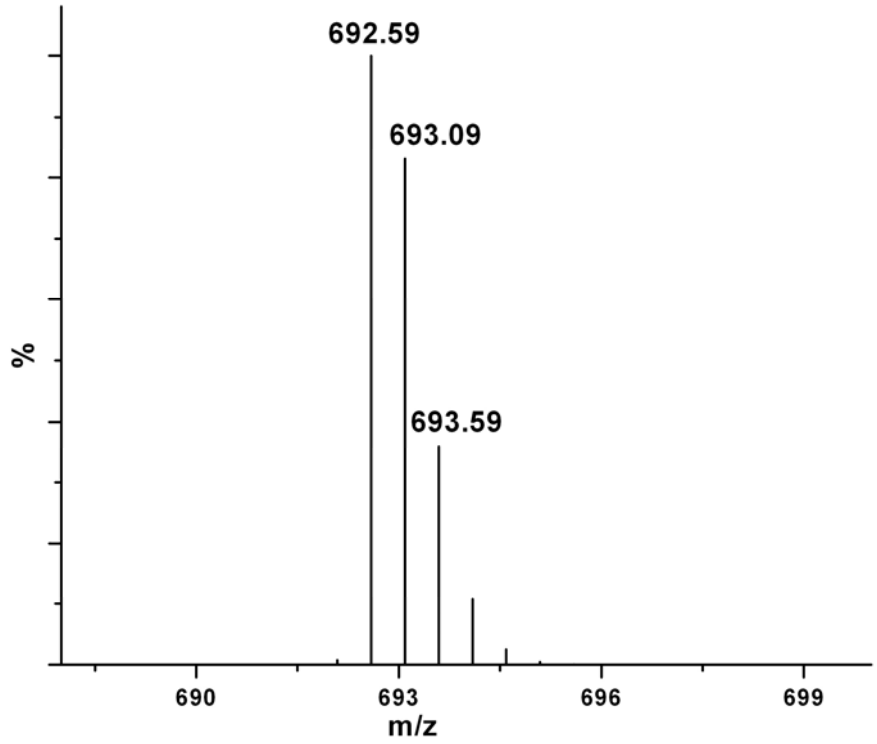


Fig. S11 Simulated ESI-MS of **4**.

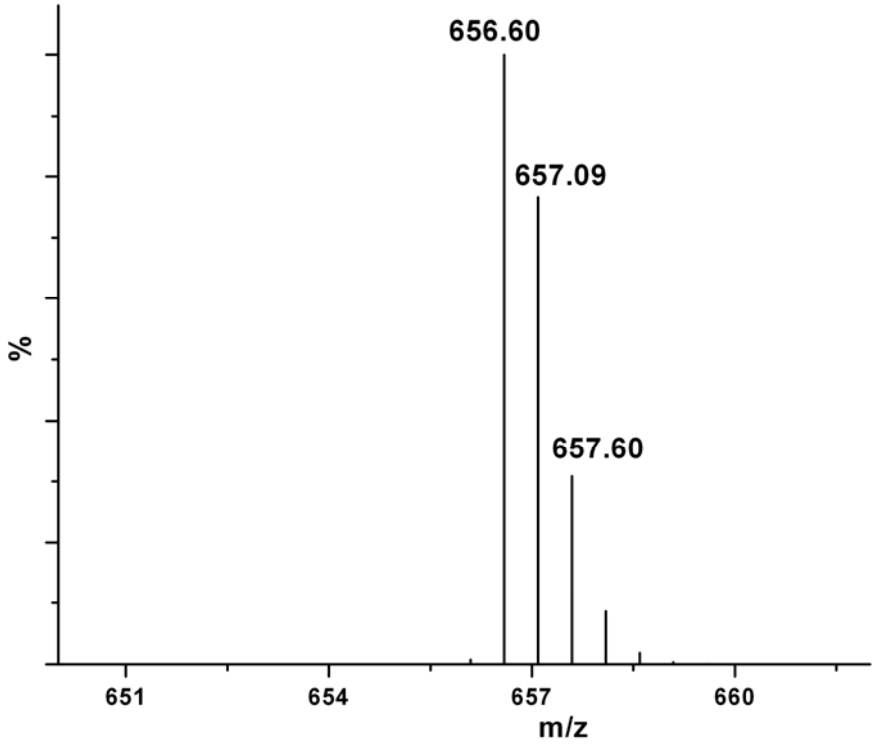


Fig. S12 Simulated ESI-MS of **5**.

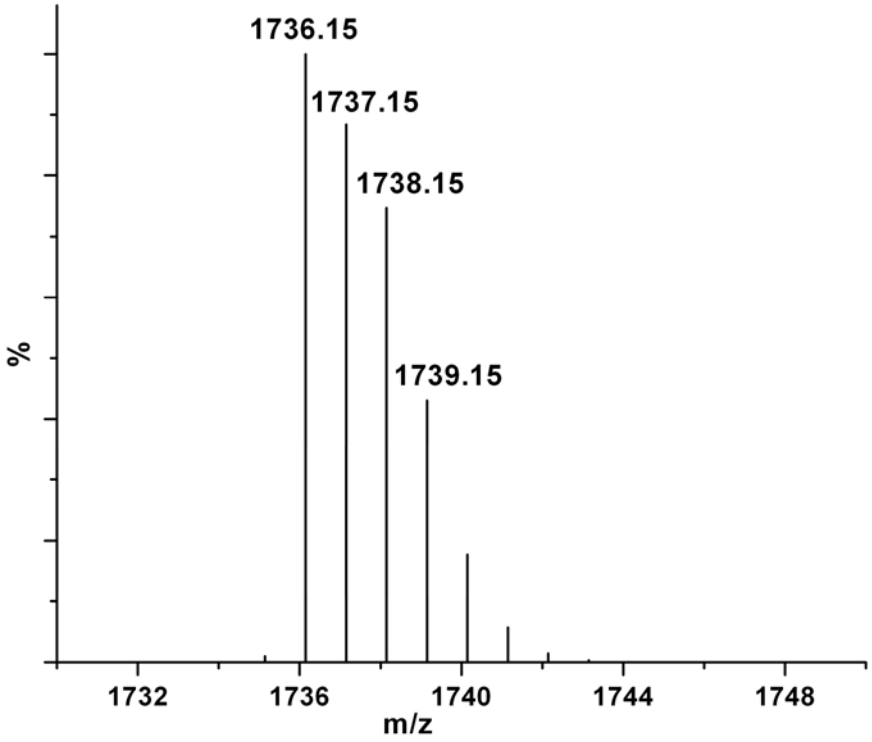
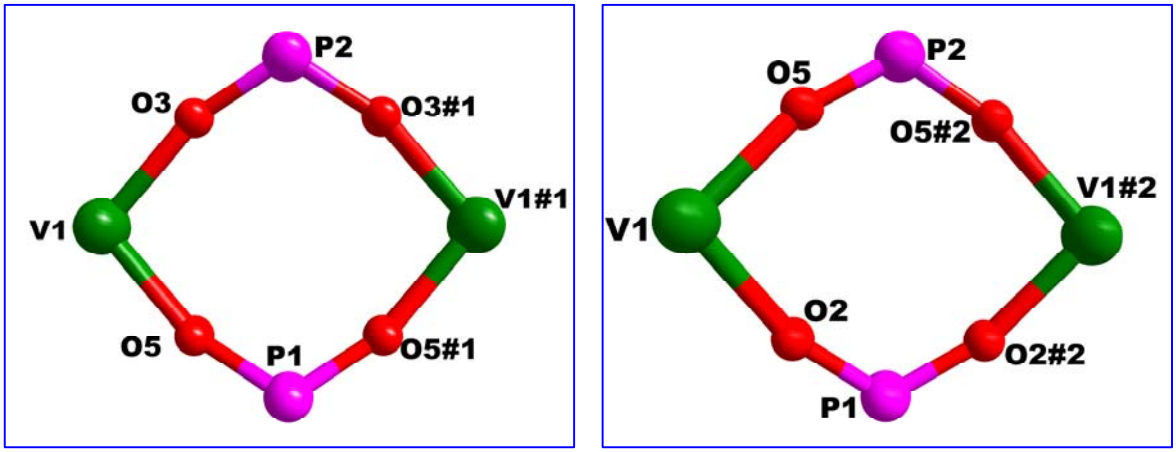


Fig. S13 Simulated ESI-MS of **6**.



(a) (b)

Fig. S14 (a) Eight-membered ($V_2P_2O_4$) puckered ring of **1**. Important bond distances (in **Å**) and angles (in deg.): V1-O3, 1.948(3); V1-O5, 1.958(4); P1-O5, 1.497(3); P2-O3, 1.499(3); O3-V1-O5, 97.89(16); P2-O3-V1, 161.0(3); P1-O5-V1, 162.9(2); O5-P1-O5$^{\#1}$, 114.7(3); O3-P2-O3$^{\#1}$, 114.7(3). **(b)** Eight-membered ($V_2P_2O_4$) puckered ring of **2**. Important bond distances (in **Å**) and angles (in deg.): V1-O2, 1.944(7); V1-O5, 1.967(8); P1-O2, 1.463(7); P2-O5, 1.455(8); O1-V1-O5, 94.5(3); P2-O5-V1, 164.2(6); P1-O2-V1, 164.3(5); O2-P1-O2$^{\#2}$, 114.4(6); O5-P2-O5$^{\#2}$, 114.3(6). Symmetry transformations used to generate equivalent atoms:#1 +X,1/2-Y,+Z; #2 +X,1/2-Y,+Z

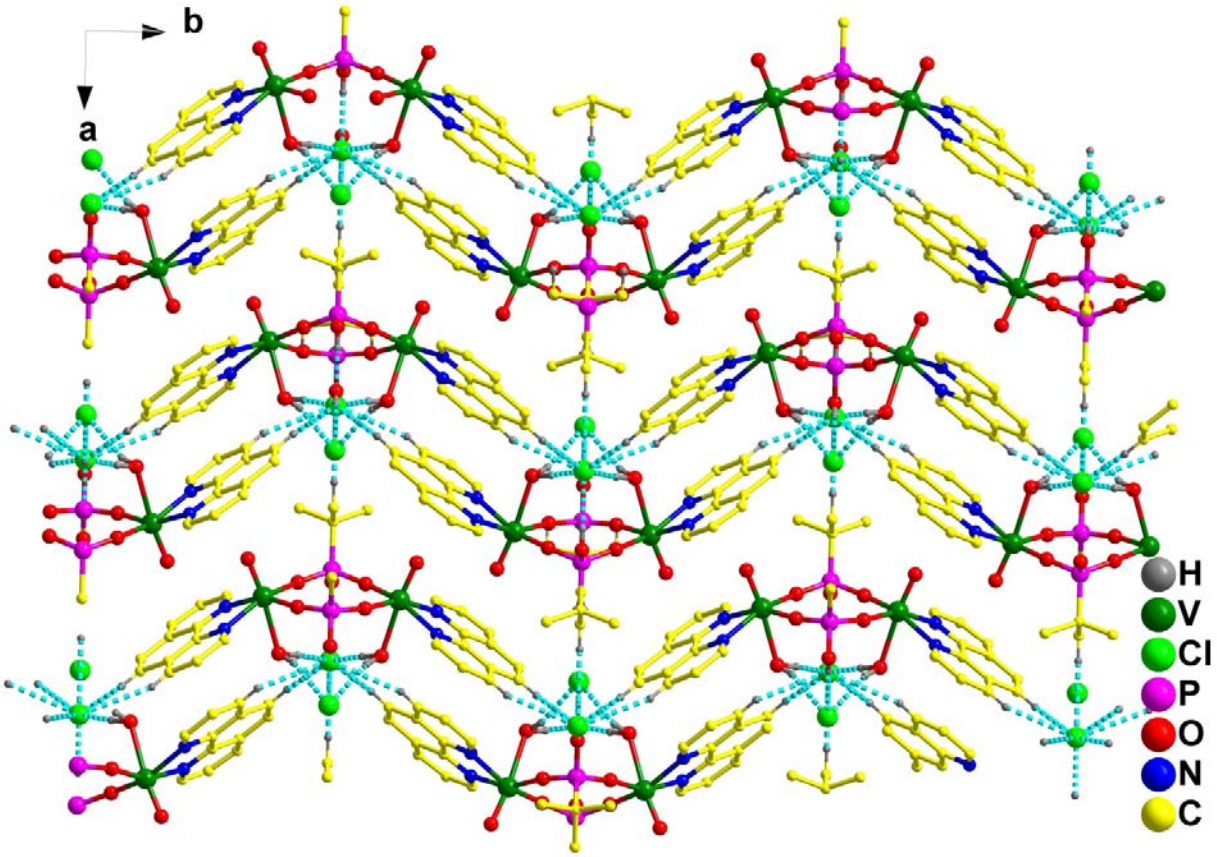


Fig. S15 Supramolecular arrangements of **1** along the *c*-axis. Some hydrogen atoms have been removed for clarity.

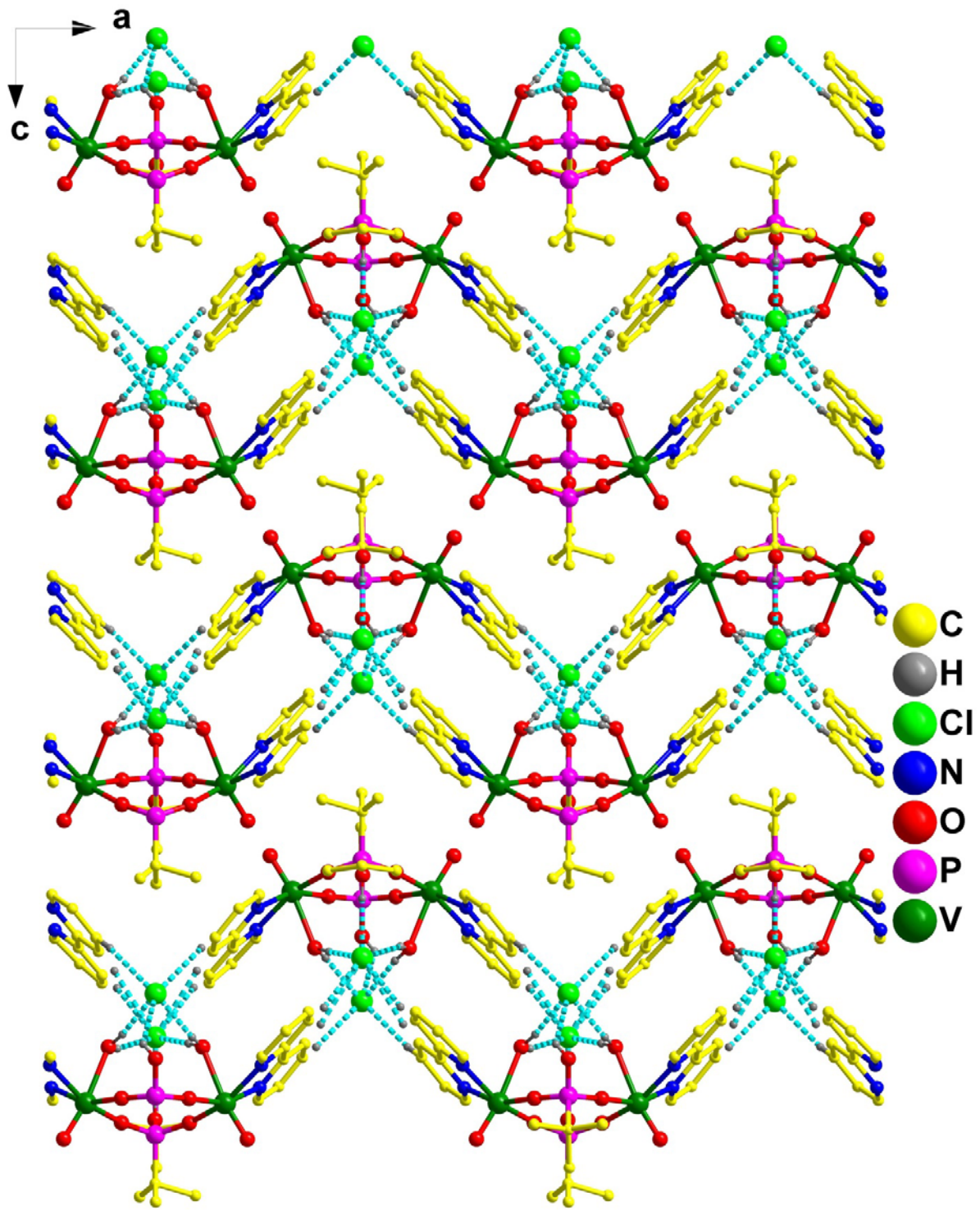


Fig. S16 Supramolecular arrangements of **2** along the *b*-axis. Some hydrogen atoms have been removed for clarity.

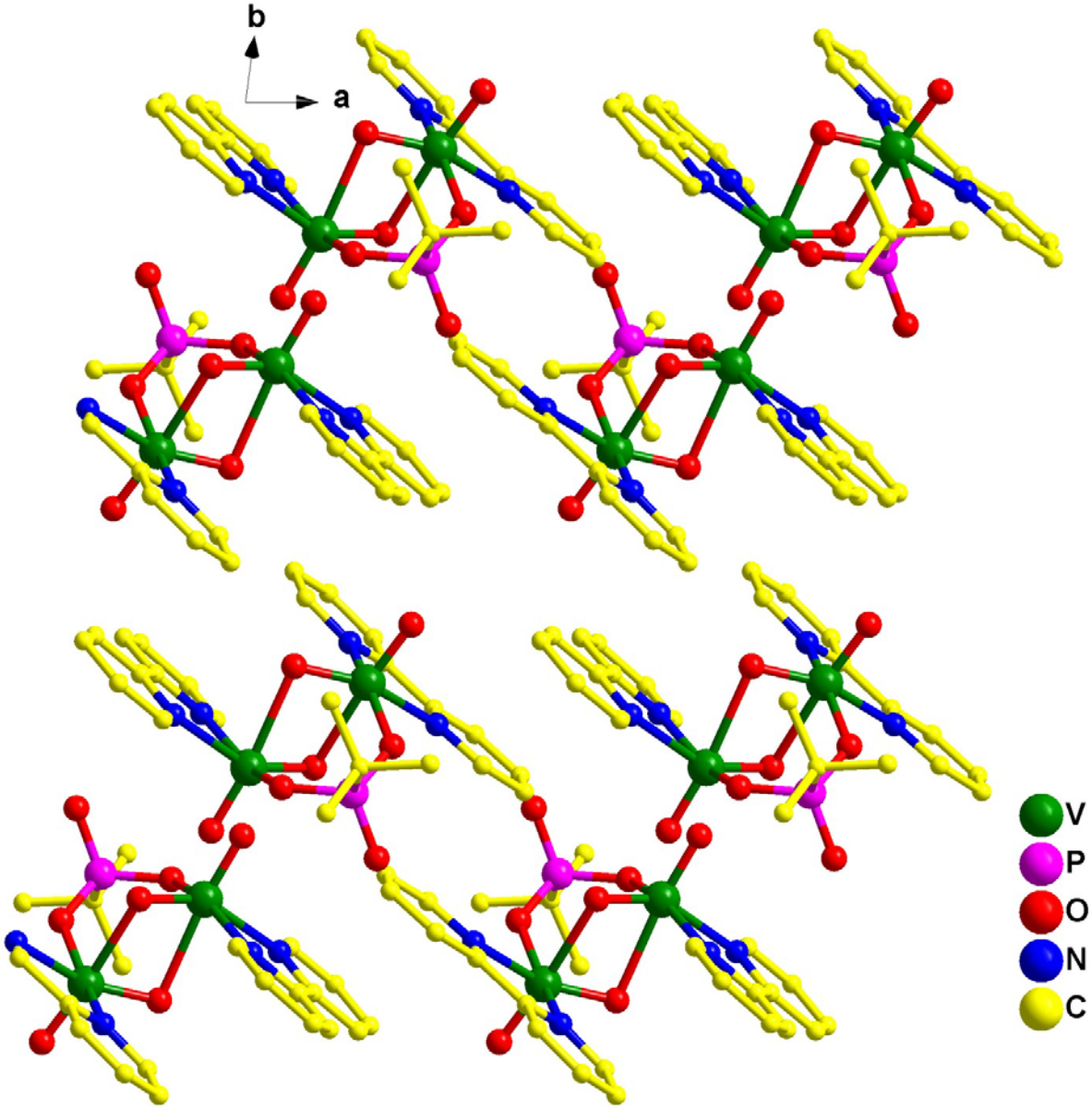


Fig. S17 Supramolecukar arrangements of **3** along the *c*-axis. Some hydrogen atoms have been removed for clarity.

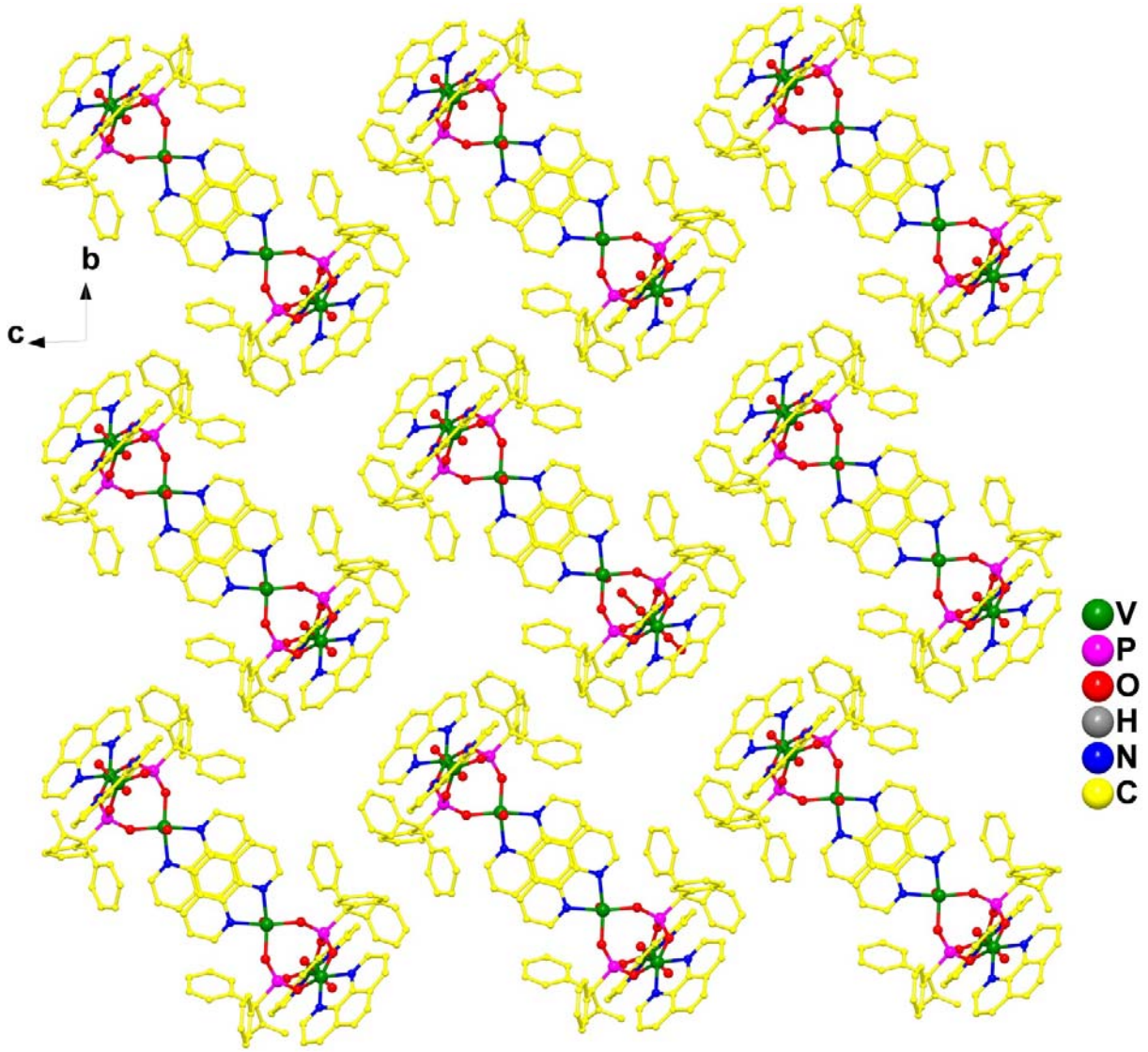


Fig. S18 Supramolecular arrangements of **4** along the *a*-axis. Some hydrogen atoms have been removed for clarity.

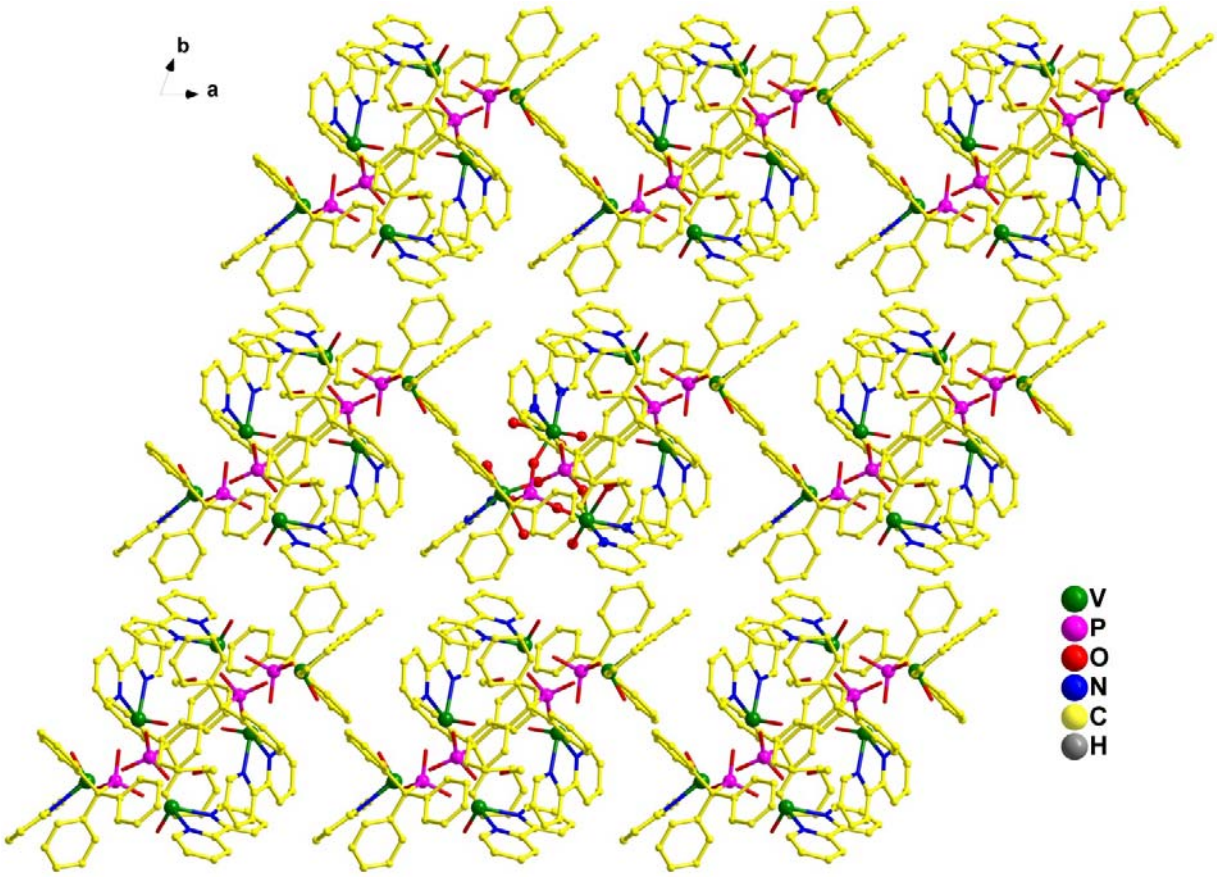


Fig. S19 Supramolecular arrangements of **5** along the *c*-axis. Some hydrogen atoms have been removed for clarity.

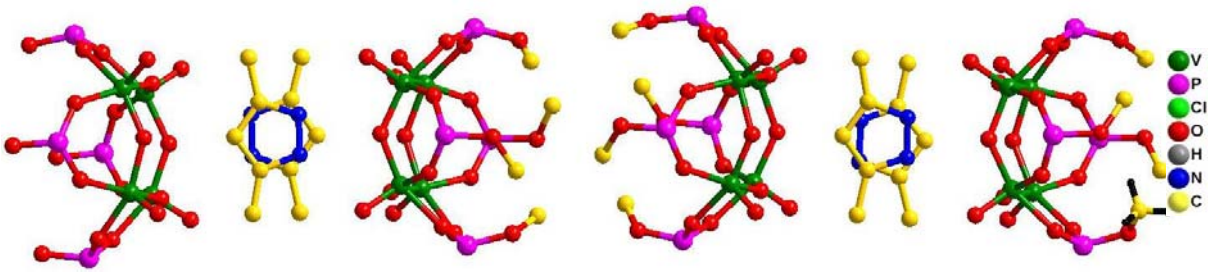


Fig. S20 Linear chain in supramolecular assembly of **6**.

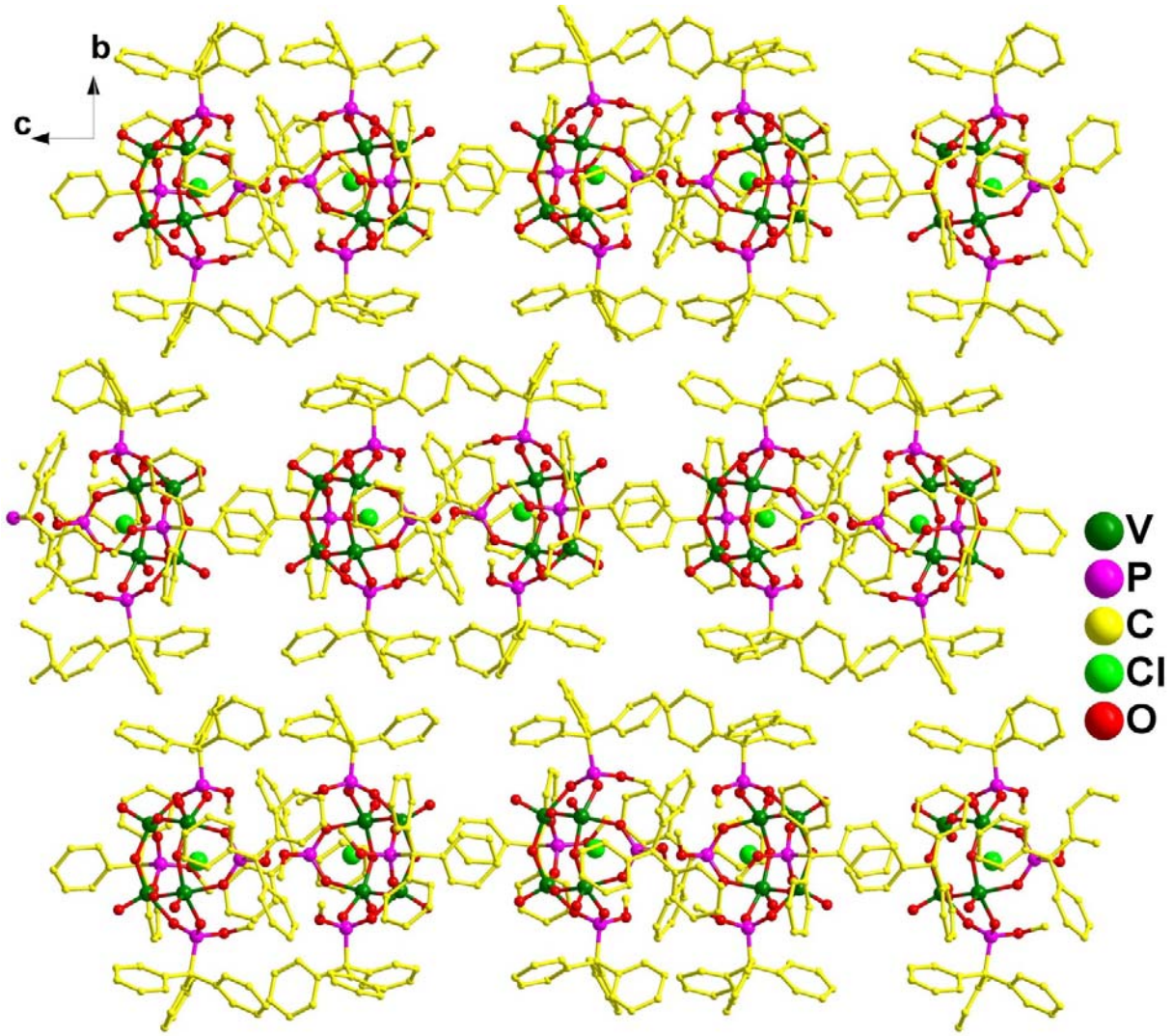


Fig. S21 Supramolecular arrangements of **6** along *a*-axis. Some hydrogen atoms have been removed for clarity.

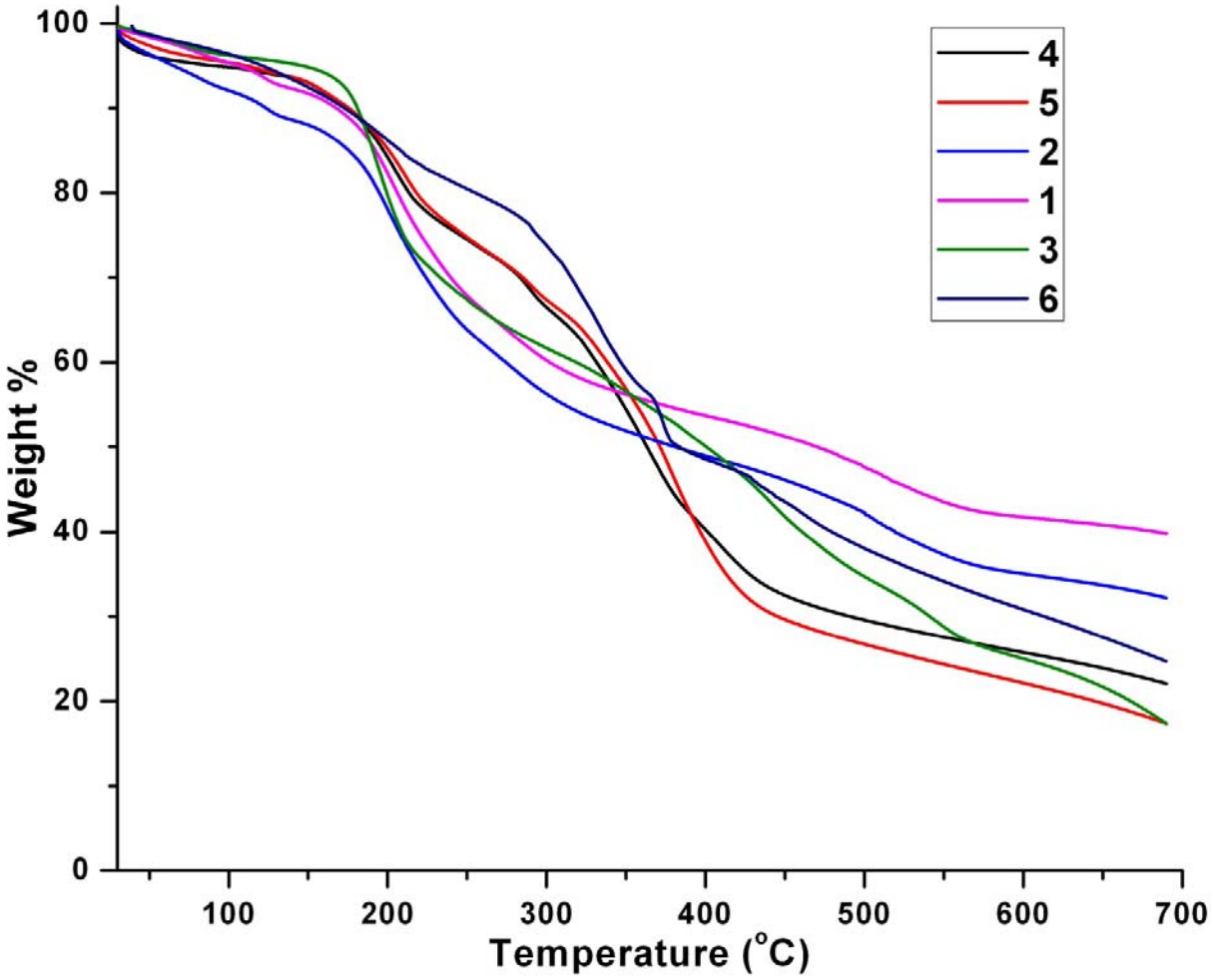
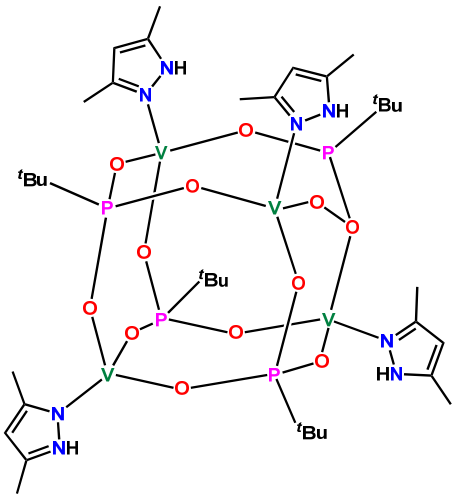
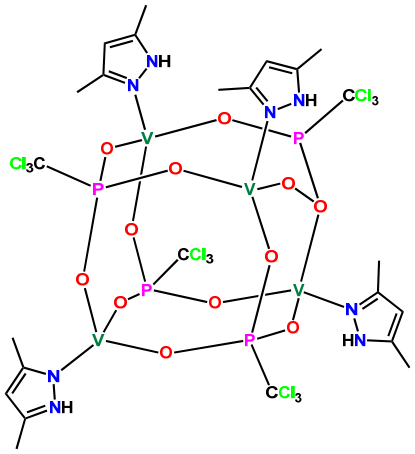


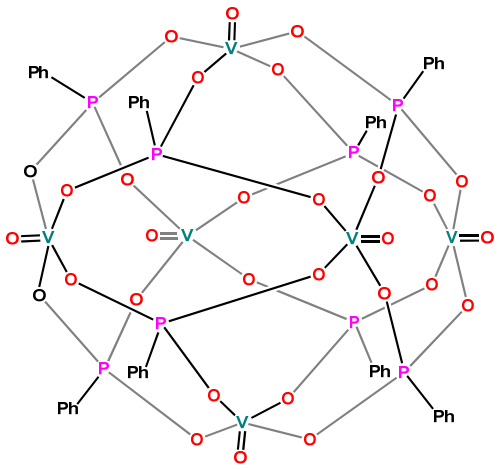
Fig. S22 Thermogrametric Analysis of **1-6**.



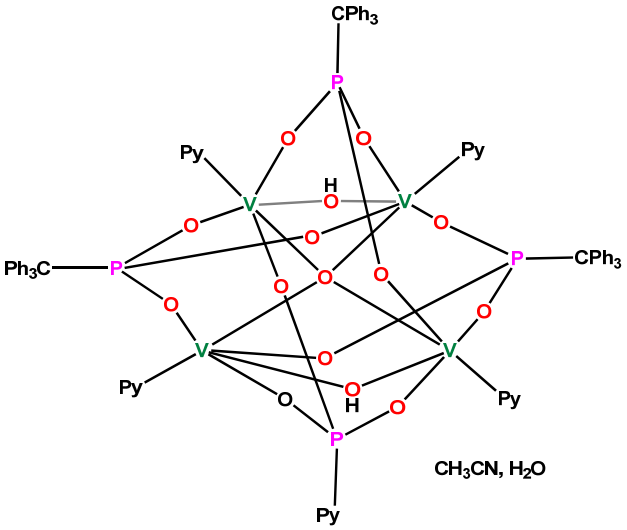
(a)



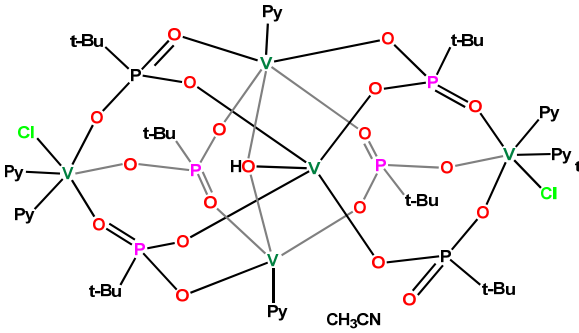
(b)



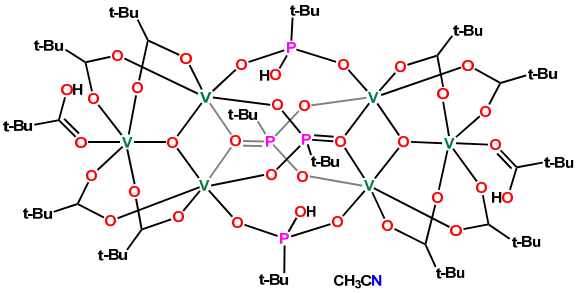
(c)


CPh3
P
O
Py
V
H
Ph3C
CPh3
CH3CN, H2O

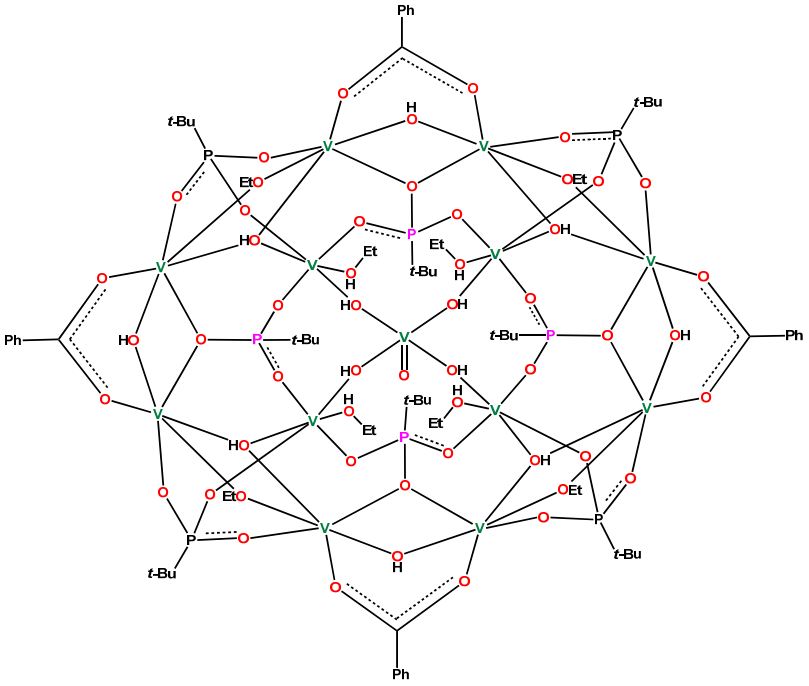
(d)


Py
t-Bu
Cl
HO
CH3CN

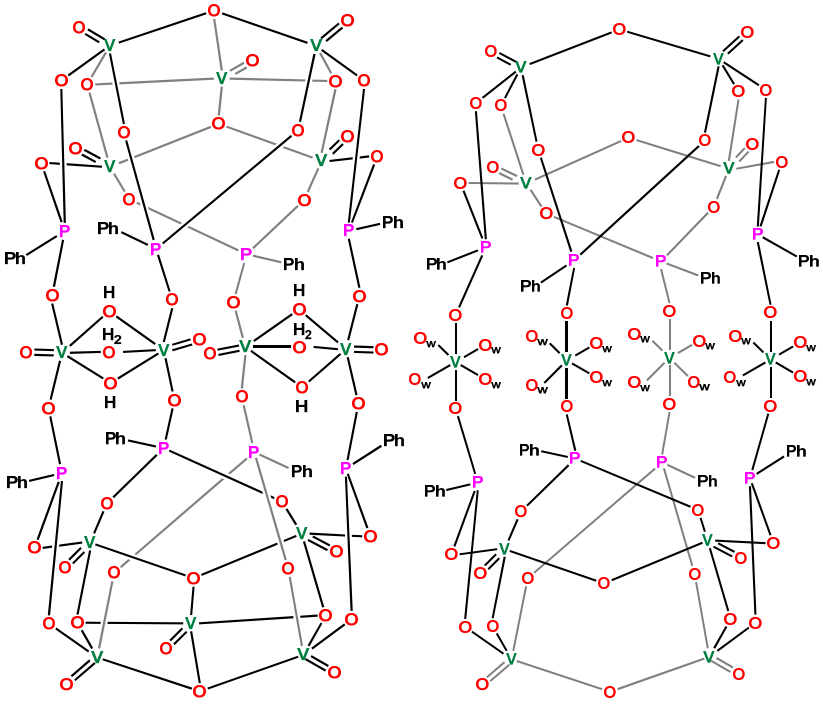
(e)


t-Bu
HO
OH
CH3CN

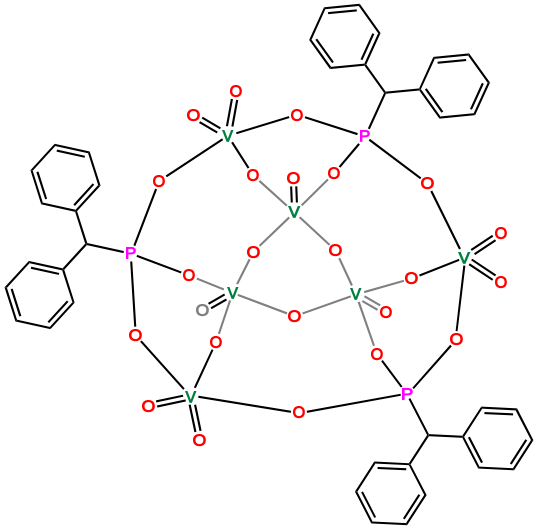
(f)



(g)



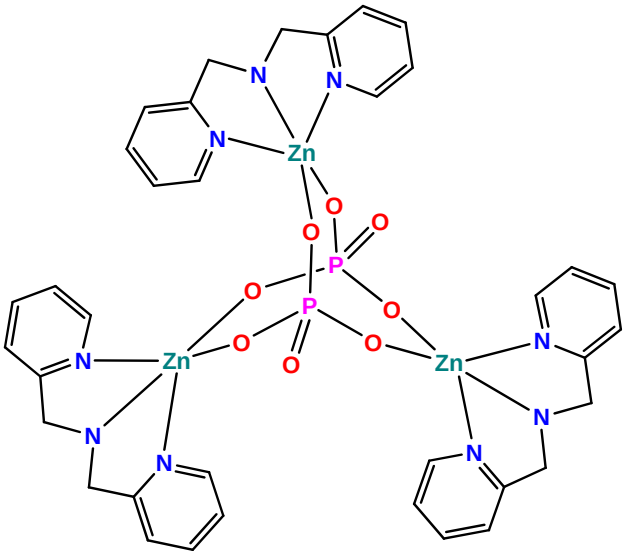
(h) (i)



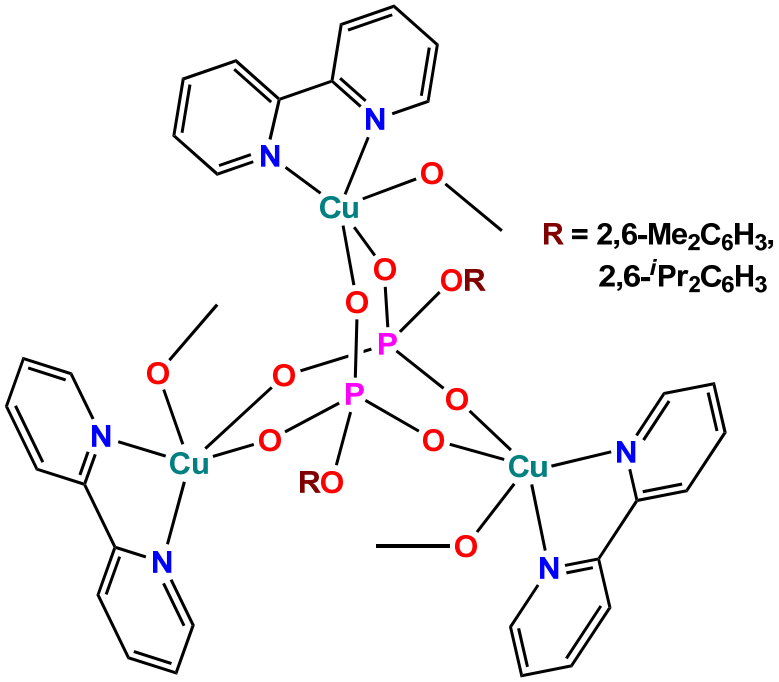
(j)

Chart S1. Representative examples of vanadium phosphonates.

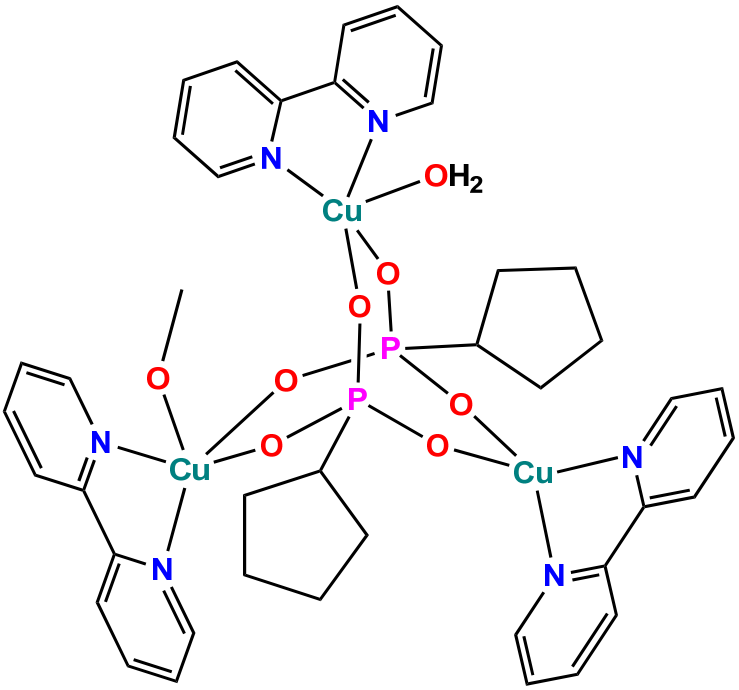
References (a) & (b) V. Chandrasekhar, A. Dey, T. Senapati and E. C. Sañudo, *Dalton Trans*., 2012, **41**, 799; (c) D. Wulff-Molder and M. *Meisel Z. Anorg. Allg. Chem*. 2008, **634**, 2966; (d), (e), (f) and (g) S. Khanra, M. Kloth, H. Mansaray, C. A. Muryn, F. Tuna, E. C. Sañudo, M. Helliwell, E. J. L. McInnes and R. E. P. Winpenny *Angew. Angew. Chem. Int. Ed*., 2007, **46**, 5568; (h) A. Muller, K. Hovemeier and R. Rohlfing *Angew. Chem. Int. Ed*. 1992, **31**, 1192; (i) Q. Chen and J.Zubieta Chem.Commun. 1994,1635; (j) S. Konar and A. Clearfield, *Inorg. Chem.*, 2008, **47**. 3492.



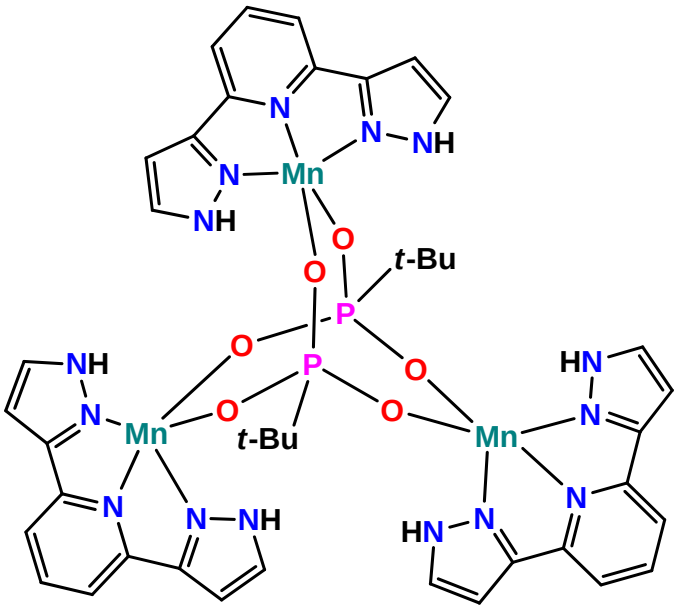
(a)



(b)


N
N
OH2
Cu
O
O
P
O
O
P
O
O
O
Cu
N
N
Cu
N
N

(c)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NH
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NH
O
O
t-Bu
P
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HN
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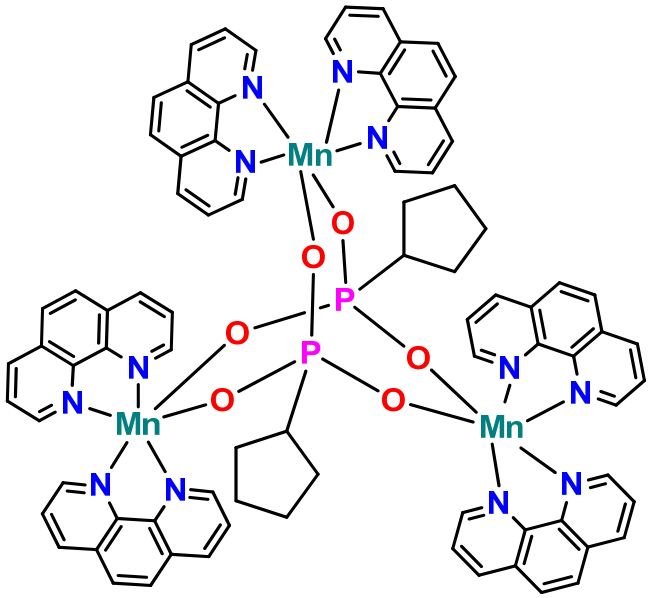
N

(d)



(e)

Chart S2. Bicapped Transition metal phosphonate cages.

References (a) F. Groß, A. Müller-Hartmann and H. Vahrenkamp, *Eur. J. Inorg. Chem*., 2000, 2363; (b) R. Murugavel, S. Kuppuswamy, A. N. Maity and M. P.Singh, *Inorg. Chem*., 2009, **48**, 183; (c) V. Chandrasekhar, T. Senapati, E. C. Sañudo and R. Clérac, *Inorg. Chem*. 2009, **48**, 6192; (d) and (e) V. Chandrasekhar, J. Goura and E. C. Sañudo, *Inorg. Chem*. 2012, **51**, 8479.

Table S1. H bonds table for **1** (Figure 2a).

Donor (D)	H atom	Acceptor (A)	D...H (in Å)	H...A (in Å)	D…A (in Å)	< D-H···A (in deg)	Symmetry Code
O2	H2B	Cl1	0.981	2.226	3.1874	166.5	x,y,-1+z
O2	H2A	Cl2	0.819	2.402	3.1915	162.0	x,y,-1+z
O4	H4	Cl1	0.796	2.188	2.9817	174.9	x,y,-1+z
O6	H6	Cl2	0.820	2.173	2.9914	176.0	x,y,-1+z

Table S2. H bonds table for **2** (Figure 2b).

Donor (D)	H atom	Acceptor (A)	Symmetry code for equiv. Pos.	D...H (in Å)	H...A (in Å)	D…A (in Å)	< D-H···A (in deg)
O1	H1	Cl1	x,y,1+z	0.820	2.360	3.049(10)	142.0
O3	H3A	Cl1	x,y,1+z	0.850	2.350	3.125(6)	151.0
O3	H3B	Cl2	-x,-1/2+y,1-z	0.850	2.390	3.156(6)	150.0
O6	H6A	Cl2	-x,-1/2+y,1-z	0.840	2.160	2.980(14)	170.0

Table S3. Hydrogen bonds parameter of **6** (Figure 11).

Donor (D)	H atom	Acceptor (A)	D...H (in Å)	H...A (in Å)	D…A (in Å)	< D-H···A (in deg)
N1	H1F	O6B	0.860	1.966	2.807	165.4
N2	H2	O11B	0.860	2.121	2.977	174.7
C39	H39	O18A	0.930	2.221	3.106	158.7
N3	H3	O6A	0.860	2.114	2.952	164.8
N4	H4B	O11A	0.859	1.947	2.805	176.0
C4Q	H4Q	O18B	0.928	2.274	3.127	152.5

Table S4. Coordination environment around the metal center for **1**.

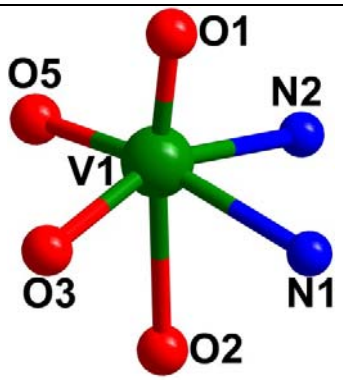
	Bond Distance (in Å)		Bond Angle (in º)	
 **Octahedral**	V1-O1	1.592(3)	N1-V1-O2	76.99(13)
	V1-O2	2.326(3)	N2-V1-O2	77.95(13)
	V1-O5	1.958(4)	O5-V1-O2	83.81(13)
	V1-O3	1.948(3)	O3-V1-O2	82.52(13)
	V1-N1	2.138(4)	O1-V1-O2	173.06(16)
	V1-N2	2.122(4)	N2-V1-N1	77.74(14)
			O5-V1-N1	158.86(14)
			O3-V1-N1	88.40(15)
			O1-V1-N1	97.23(17)
			O5-V1-N2	89.77(15)
			O3-V1-N2	158.12(14)
			O1-V1-N2	97.17(16)
			O3-V1-O5	97.89(16)
			O1-V1-O5	101.24(17)
			O1-V1-O3	101.34(16)

Table S5. Coordination environment around the metal center for **2**.

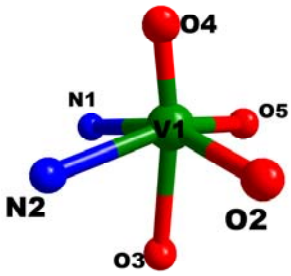
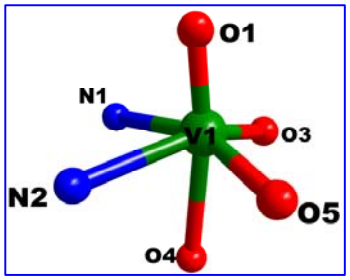
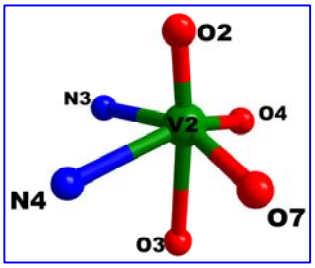
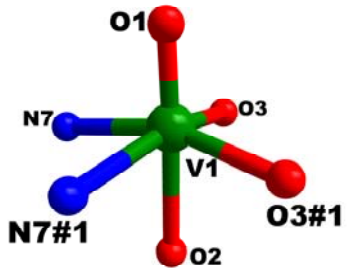
	Bond Distance (in Å)		Bond Angle (in º)	
 **Octahedral**	V1-O2	1.967(7)	O2-V1-O3	83.9(3)
	V1-O3	2.288(6)	O2-V1-O4	103.2(3)
	V1-O4	1.584(7)	O2-V1-N1	89.9(3)
	V1-O5	1.943(8)	O2-V1-N2	158.4(3)
	V1-N1	2.114(6)	O4-V1-O5	101.5(3)
	V1-N2	2.116(8)	O4-V1-O3	170.5(3)
			O4-V1-N1	97.6(3)
			O4-V1-N2	95.6(3)
			O3-V1-O5	84.0(3)
			O5-V1-N1	158.8(3)
			O5-V1-N2	91.8(3)
			N1-V1-O3	75.8(2)
			N2-V1-O3	76.3(3)
			N1-V1-N2	77.2(3)

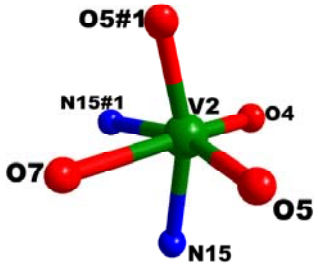
Table S6. Coordination environment around the metal center for **3**.

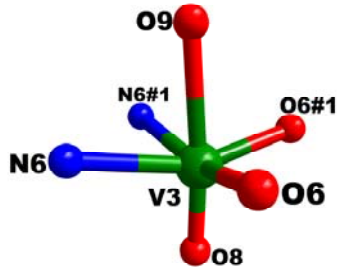
	Bond Distance (in Å)		Bond Angle (in º)	
 **Octahedral**	V1-O3	1.670(4)	O1-V1-O3	107.1(2)
	V1-O5	1.902(5)	O3-V1-O5	102.7(2)
	V1-O1	1.624(4)	O1-V1-N2	95.1(2)
	V1-O4	2.335(4)	O3-V1-N2	153.9(2)
	V1-N1	2.130(6)	O5-V1-N2	85.9(2)
	V1-N2	2.207(6)	O1-V1-N1	92.9(2)
			O3-V1-N1	91.1(2)
			O5-V1-N1	156.2(2)
			N1-V1-N2	73.8(2)
			O1-V1-O4	170.9(2)
			O3-V1-O4	80.54(18)
			O5-V1-O4	81.51(18)
			N2-V1-O4	76.36(17)
			N1-V1-O4	81.74(18)
			O1-V1-O5	101.3(2)
 **Octahedral**	V2-O2	1.621(5)	O2-V2-O3	173.76(2)
	V2-O7	1.929(5)	O2-V2-O4	106.4(2)
	V2-N4	2.217(6)	O2-V2-O7	102.1(2)
	V2-O3	2.432(4)	O2-V2-N3	93.0(2)
	V2-N3	2.141(6)	O2-V2-N4	100.1(2)
	V2-O4	1.652(5)	O4-V2-O7	101.0(2)

		O4-V2-O3	77.87(19)
		O4-V2-N3	91.1(2)
		O4-V2-N4	149.8(2)
		N3-V2-N4	73.4(2)
		O7-V2-O3	81.16(17)
		O7-V2-N3	157.0(2)
		O7-V2-N4	86.8(2)
		N3-V2-O3	82.36(17)
		N4-V2-O3	74.62(16)

Table S7. Coordination environment around the metal center for **4**.

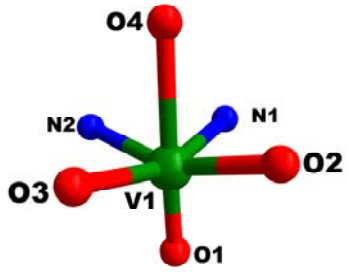
	Bond Distance (in Å)	Bond Angle (in º)	
 **Octahedral**	V1-O1 1.593(6)	O1-V1-O2	177.8(3)
	V1-O2 2.291(6)	O1-V1-N7	97.4(2)
	V1-O3 1.967(4)	O1-V1-N7$^{\#1}$	97.4(2)
	V1-O3$^{\#1}$ 1.967(4)	O1-V1-O3	101.01(18)
	V1-N7 2.101(5)	O1-V1-O3$^{\#1}$	101.01(18)
	V1-N7$^{\#1}$ 2.101(5)	O3-V1-O2	80.49(15)
		O3-V1-O3$^{\#1}$	94.1(2)
		O3-V1-N7	91.39(17)
		O3-V1-N7$^{\#1}$	159.38(18)

		$O3^{\#1}$-V1-N7 159.38(18) $O3^{\#1}$-V1-$N7^{\#1}$ 91.39(17) $O3^{\#1}$-V1-O2 80.48(15) N7-V1-$N7^{\#1}$ 77.0(2) N7-V1-O2 80.85(18) $N7^{\#1}$-V1-O2 80.85(18)
 **Octahedral**	V2-O4 1.617(6) V2-O5 1.951(4) V2-$O5^{\#1}$1.974(4) V2-O7 2.238(6) V2-N15 2.108(6) V2-$N15^{\#1}$2.107(6)	O4-V2-O5 100.38(18) O4-V2-$O4^{\#1}$ 100.38(18) O4-V2-O7 175.3(3) O4-V2-N15 94.3(2) O4-V2-$N15^{\#1}$ 94.3(2) O5-V2-$O5^{\#1}$ 96.8(2) O5-V2-O7 82.67(18) O5-V2-N15 90.17(19) O5-V2-$N15^{\#1}$ 162.3(2) $O5^{\#1}$-V2-N15 162.3(2) $O5^{\#1}$-V2-$N15^{\#1}$90.17(19) $O5^{\#1}$-V2-O7 82.67(18) N15-V2-$N15^{\#1}$78.8(3) N15-V2-O7 82.1(2)

 **Octahedral**	V3-O6 1.945(4) V3-O6$^{\#1}$1.945(4) V3-O8 1.595(7) V3-O9 2.293(6) V3-N6 2.126(5) V3-N6$^{\#1}$2.126(5)	O6-V3-O$^{\#1}$ 95.7(2) O6-V3-O9 81.90(16) O6-V3-N6 89.96(17) O6-V3-N6$^{\#1}$ 157.98(19) O6$^{\#1}$-V3-O9 81.90(16) O6$^{\#1}$-V3-N6 89.96(17) O6$^{\#1}$-V3-O8 101.64(19) O8-V3-O9 174.6(3) O8-V3-N6 98.0(2) O8-V3-N6$^{\#1}$ 98.0(2) N6-V3-N6$^{\#1}$ 77.5(3) N6-V3-O9 77.86(19) N6$^{\#1}$-V3-O9 77.86(19)

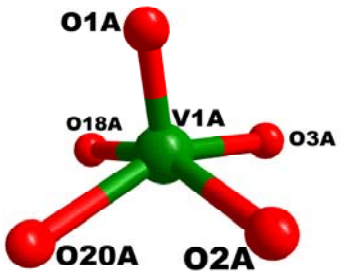
Symmetry transformations used to generate equivalent atoms: +X,1-Y,+Z

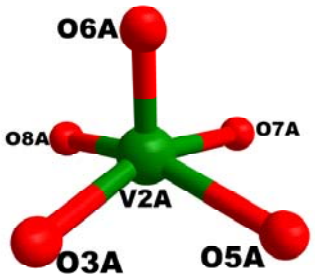
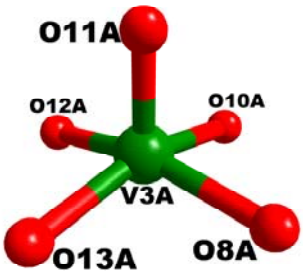
Table S8. Coordination environment around the metal center for **5**.

	Bond Distance (in **Å**)	Bond Angle (in **º**)
 **Octahedral**	V1-O1 1.589(7) V1-O2 1.949(7) V1-O3 1.952(7) V1-O4 2.321(6) V1-N1 2.096(9) V1-N2 2.119(8)	O1-V1-O2 101.5(3) O1-V1-O3 101.2(3) O1-V1-O4 176.7(3) O1-V1-N1 96.8(3) O1-V1-N2 98.8(3) O2-V1-O3 95.3(3) O2-V1-O4 78.8(3)

		O2-V1-N2 157.0(3) O2-V1-N1 90.9(3) O3-V1-O4 82.0(3) O3-V1-N1 159.4(3) O3-V1-N2 91.0(3) N1-V1-O4 79.9(3) N2-V1-O4 80.2(3) N1-V1-N2 76.2(3)

Table S9. Coordination environment around the metal center for **6**.

	Bond distances (in Å)	Bond angles (in °)
 **Square pyramidal**	V1A-O1A 1.576(5) V1A-O2A 1.941(5) V1A-O3A 1.796(5) V1A-O18A 1.878(5) V1A-O20A 1.984(5)	O1A-V1A-O2A 100.1(2) O1A-V1A-O3A 102.3(2) O1A-V1A-O18A 100.9(2) O1A-V1A-O20A 101.4(2) O2A-V1A-O3A 88.6(2) O2A-V1A-O18A 157.7(2) O2A-V1A-O20A 82.82(19) O3A-V1A-O18A 94.1(2) O3A-V1A-O20A 155.9(2) O18A-V1A-O20A 85.8(2)
	V2A-O3A 1.848(5)	O3A-V2A-O5A 87.86(19)

 **Square pyramidal**	V2A-O5A	1.985(5)	O3A-V2A-O6A	99.5(2)
	V2A-O6A	1.597(5)	O3A-V2A-O7A	160.0(2)
	V2A-O7A	1.974(5)	O3A-V2A-O8A	94.7(2)
	V2A-O8A	1.802(5)	O5A-V2A-O6A	101.8(2)
			O5A-V2A-O7A	81.88(19)
			O5A-V2A-O8A	157.0(2)
			O6A-V2A-O7A	99.5(2)
			O6A-V2A-O8A	100.3(2)
			O7A-V2A-O8A	88.4(2)
 **Square pyramidal**	V3A-O8A	1.847(5)	O8A-V3A-O10A	86.9(2)
	V3A-O10A	1.993(5)	O8A-V3A-O11A	98.8(2)
	V3A-O11A	1.592(5)	O8A-V3A-O12A	157.9(2)
	V3A-O12A	1.946(5)	O8A-V3A-O13A	93.9(2)
	V3A-O13A	1.806(5)	O10A-V3A-O11A	101.1(2)
			O10A-V3A-O12A	82.1(2)
			O10A-V3A-O13A	156.4(2)
			O11A-V3A-O12A	102.1(2)
			O11A-V3A-O13A	102.1(2)
			O12A-V3A-O13A	88.7(2)
	V4A-O13A	1.835(5)	O13A-V4A-O15A	87.4(2)
	V4A-O15A	1.989(5)	O13A-V4A-O16A	101.1(2)
	V4A-O16A	1.585(5)	O13A-V4A-O17A	157.1(2)
	V4A-O17A	1.966(5)	O13A-V4A-O18A	94.7(2)

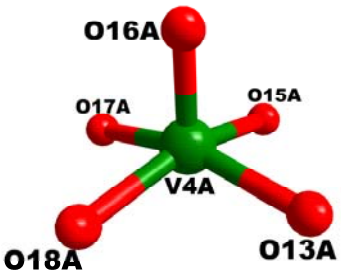
 **Square pyramidal**	V4A-O18A 1.818(5)	O15A-V4A-O16A 100.5(2) O15A-V4A-O17A 82.94(19) O15A-V4A-O18A 157.6(2) O16A-V4A-O17A 101.0(2) O16A-V4A-O18A 100.9(2) O17A-V4A-O18A 86.8(2)

Table S10. BVS Calculation for **1**.

Atom	BVS
V1	3.94 ≈ 4

Table S11. BVS Calculation for **2**.

Atom	BVS
V1	4.05 ≈ 4
V2	4.03 ≈ 4

Table S12. BVS Calculation for **3**.

Atom	BVS
V1	4.97 ≈ 5
V2	4.93 ≈ 5

Table S13. BVS Calculation for **4**.

Atom	BVS
V1	3.98 ≈ 4
V2	3.95 ≈ 4
V3	3.99 ≈ 4

Table S14. BVS Calculation for **5**.

Atom	BVS
V1	3.97 ≈ 4
V2	4.00 ≈ 4
V3	3.94 ≈ 4

Table S15. BVS Calculation for **6**.

Atom	BVS
V1	4.97 ≈ 5
V2	4.84 ≈ 5
V3	4.83 ≈ 5
V4	4.82 ≈ 5