Supporting Information

Spontaneous conversions of glutamine, histidine and arginine to α-hydroxycarboxylates with NH_4VO_3 or V_2O_5

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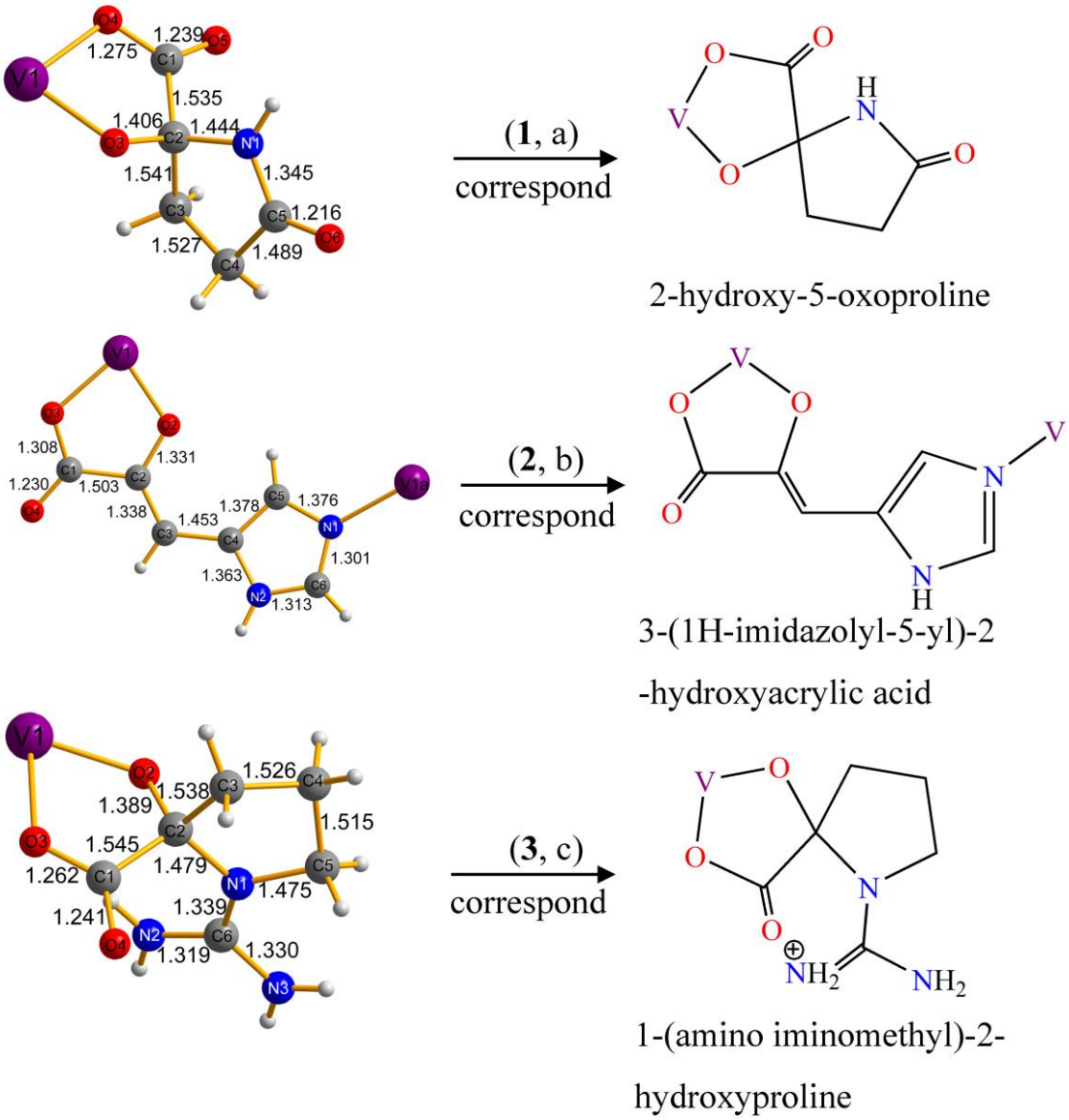
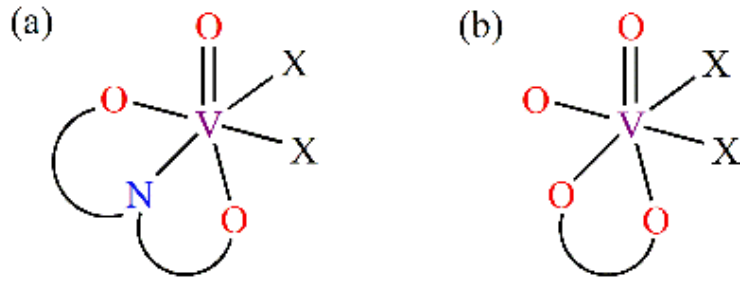


Scheme S1. Structures confirmation of α-hydroxycarboxylates in $[V^{V}_2O_3(hop)_2(bpy)_2]\cdot 7H_2O$ (**1**, a), $[V^{IV}_2O_2(imha)_2(bpy)_2]\cdot bpy$ (**2**, b) and $(CN_3H_6)[V^{V}O_2(Haimhp)_2]\cdot 2H_2O$ (**3**, c).



Scheme S2. (a) Some similar amino acid-derivatized vanadium complexes. (b) Schematic diagram of the structures **1** ~ **3**. X = H_2O, 2,2′-bipyridine, 1,10-phenanthroline or some other nitrogen-containing, oxygen-containing ligands.

Structural comparison with VHPOs. Comparisons of **1** ~ **3** with the other glycine/L-alanine/L-valine/L-leucine/L-histidine/L-threonine–salicylaldehyde derivatives as model compounds for haloperoxidases are shown in Scheme S2. We can find that ligands in **1** ~ **3** have been converted to α-hydroxycarboxylates and N atoms do not coordinate with vanadium in Scheme S2b, which differ from other reported amino acid-derivatized vanadium complexes in Scheme S2a.[1-4]

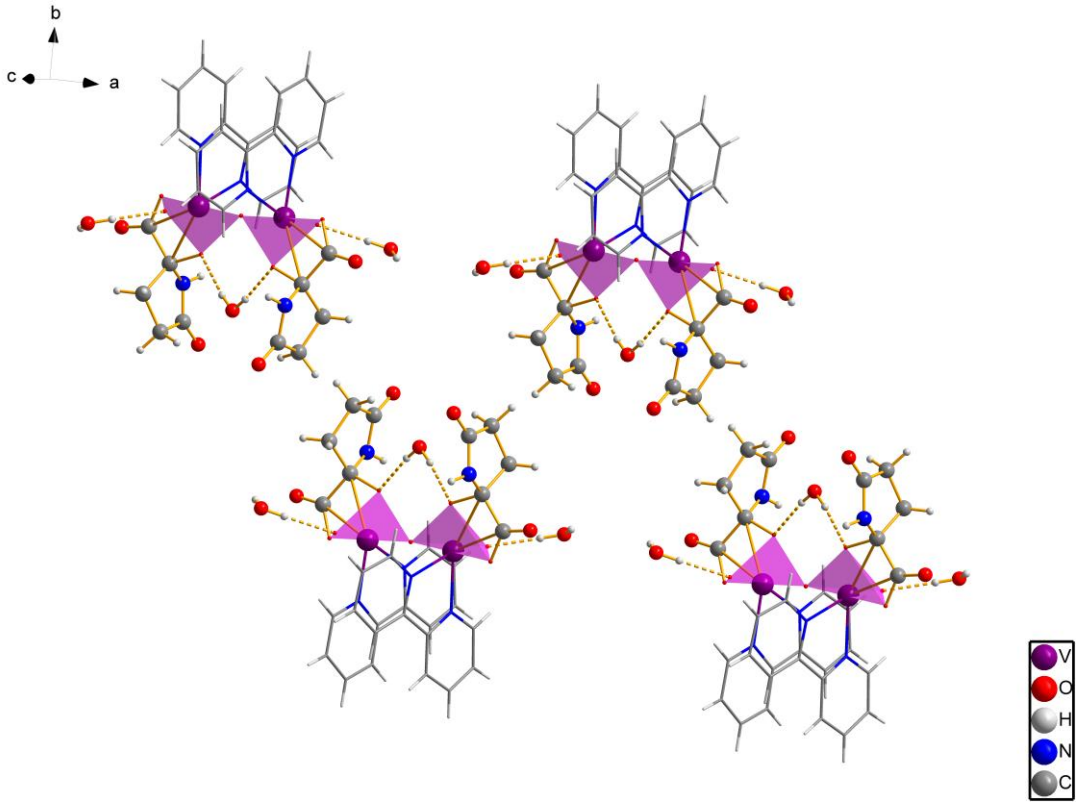


Figure S1. 3D layered diagram of the molecular structure in $[V^{V}_{2}O_{3}(hop)_{2}(bpy)_{2}]\cdot 7H_{2}O$ (**1**).

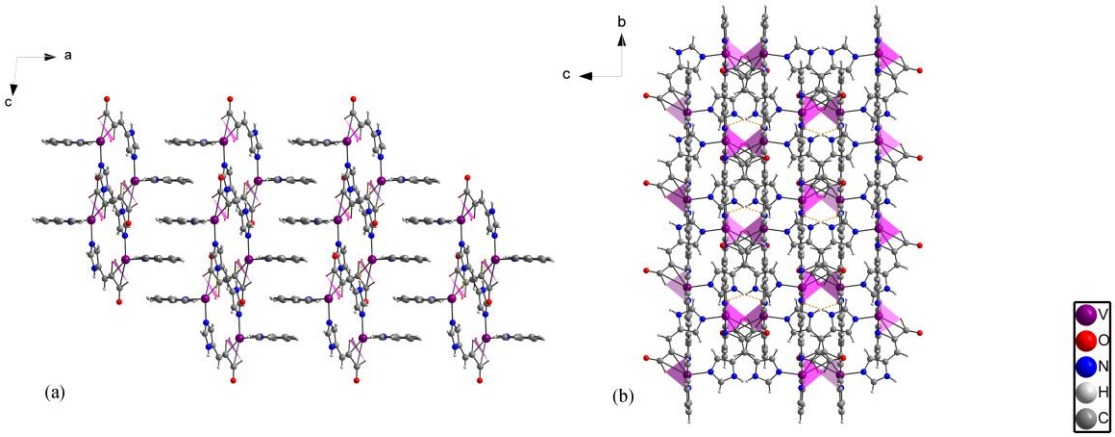


Figure S2. 3D layered diagram of the molecular structure in $[V^{IV}_2O_2(imha)_2(bpy)_2]\cdot bpy$ (**2**), free disordered 2,2′-bipyridine molecules are omitted for clarity. View along the (a) *b* and (b) *a* axes. The thick yellow dotted lines represent hydrogen bonds [N2 ··O1].

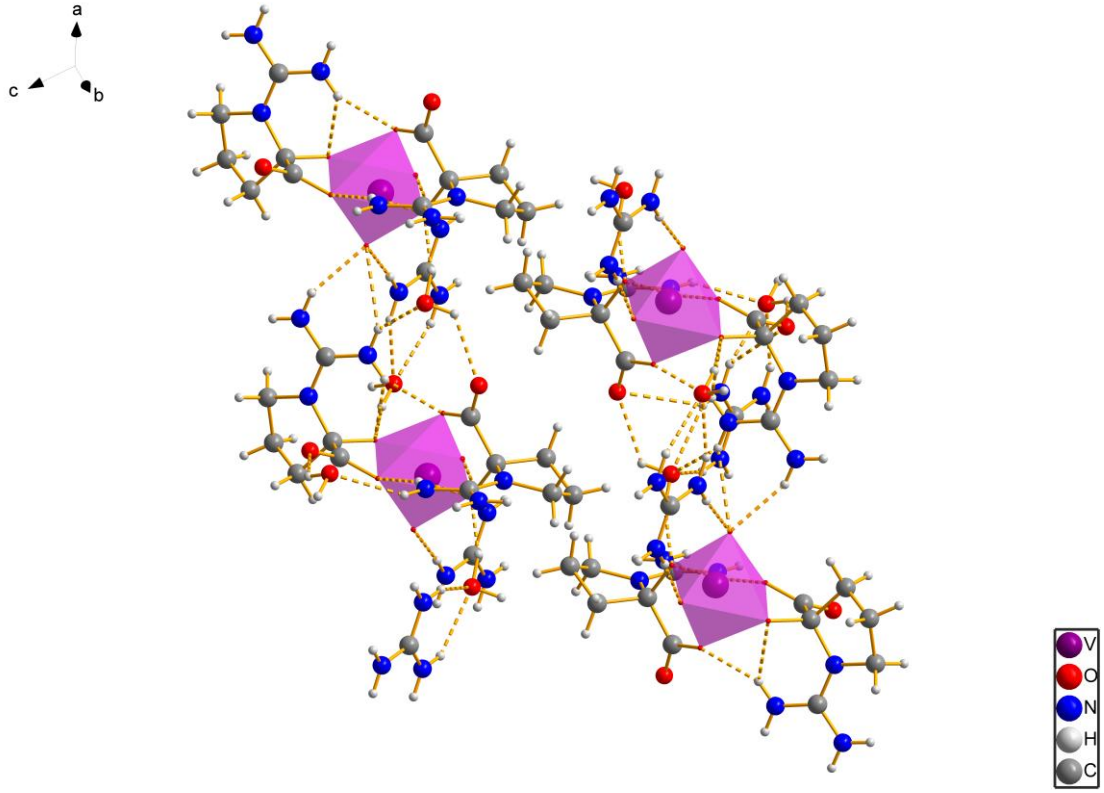


Figure S3. 3D layered diagram of the molecular structure in $(CN_3H_6)[V^{V}O_2(Haimhp)_2]\cdot 2H_2O$ (**3**).

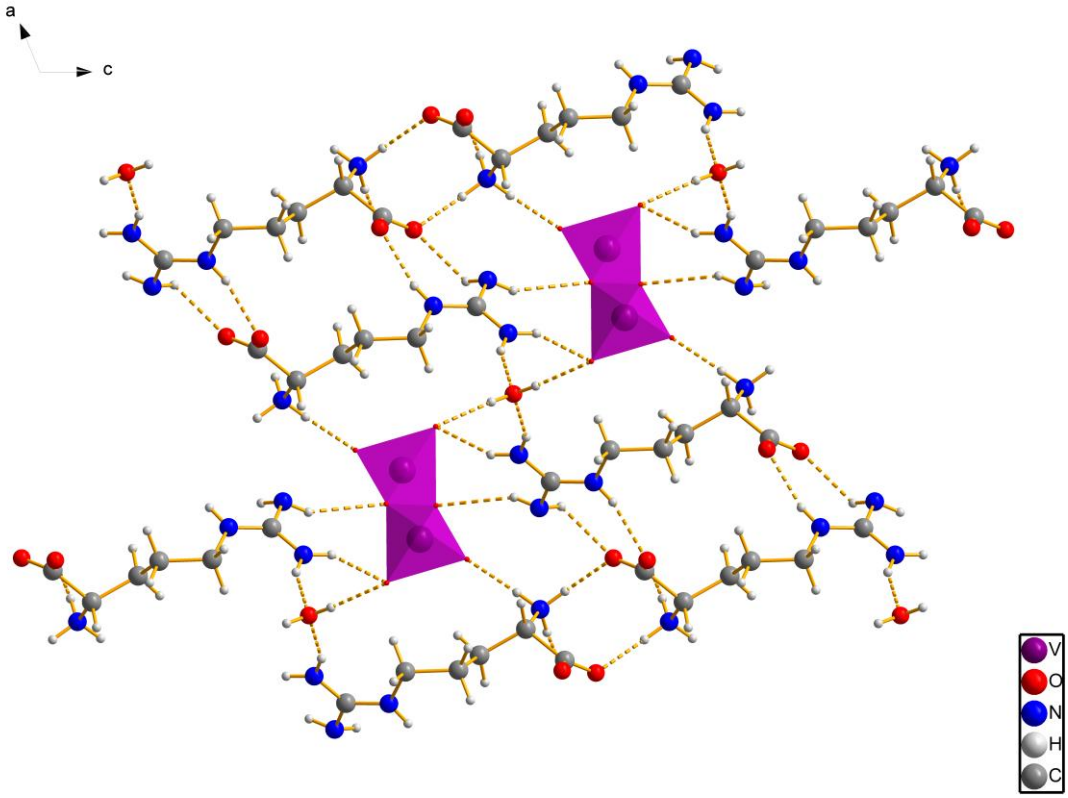


Figure S4. 3D layered diagram of the molecular structure in $(H_2arg)_n(V^VO_3)_n$ ½nH_2O (**4**).

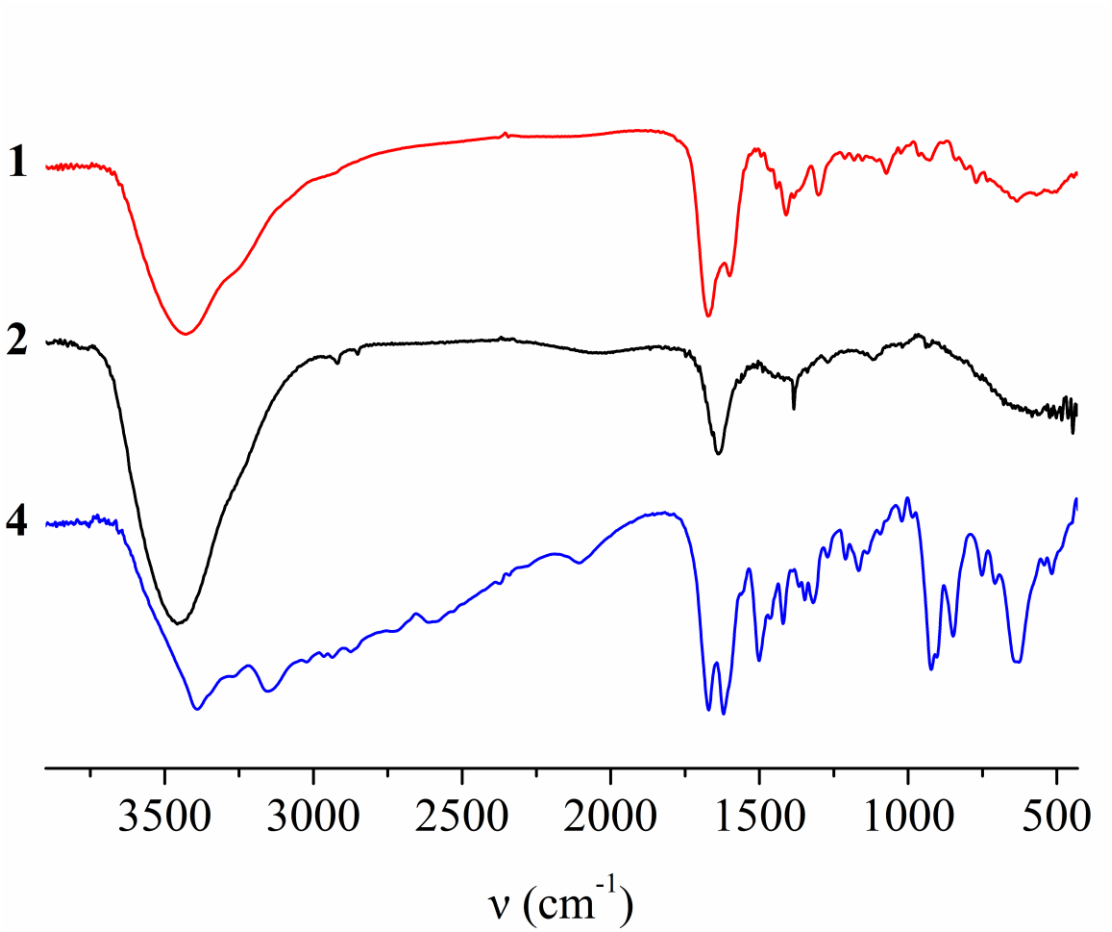


Figure S5. IR spectra of $[V^{V}_{2}O_{3}(hop)_{2}(bpy)_{2}]\cdot 7H_{2}O$ (**1**), $[V^{IV}_{2}O_{2}(imha)_{2}(bpy)_{2}]\cdot bpy$ (**2**) and $(H_{2}arg)_{n}(V^{V}O_{3})_{n}$ ½n$H_{2}O$ (**4**).

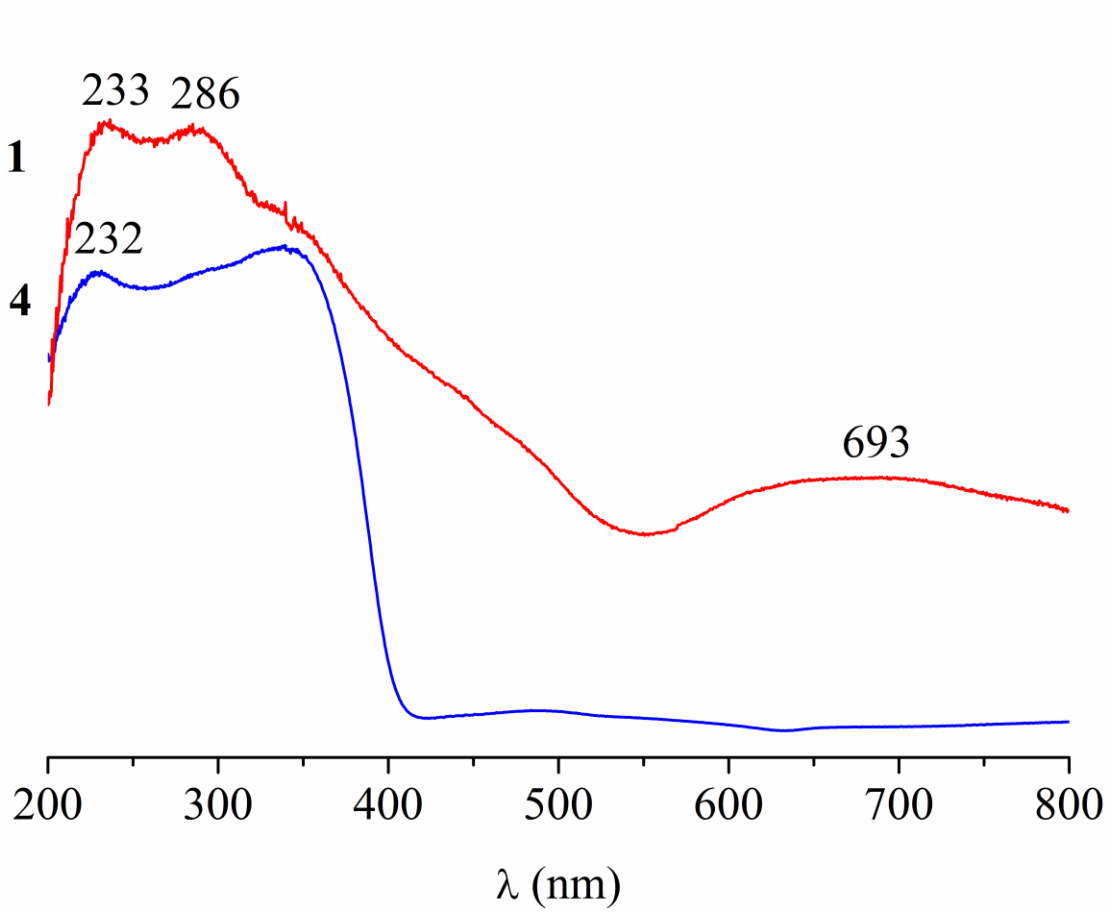


Figure S6. Diffused reflectance spectra of solids $[V^{V}_{2}O_{3}(hop)_{2}(bpy)_{2}]\cdot 7H_{2}O$ (**1**), $(H_{2}arg)_{n}(V^{V}O_{3})_{n}$ ½n$H_{2}O$ (**4**).

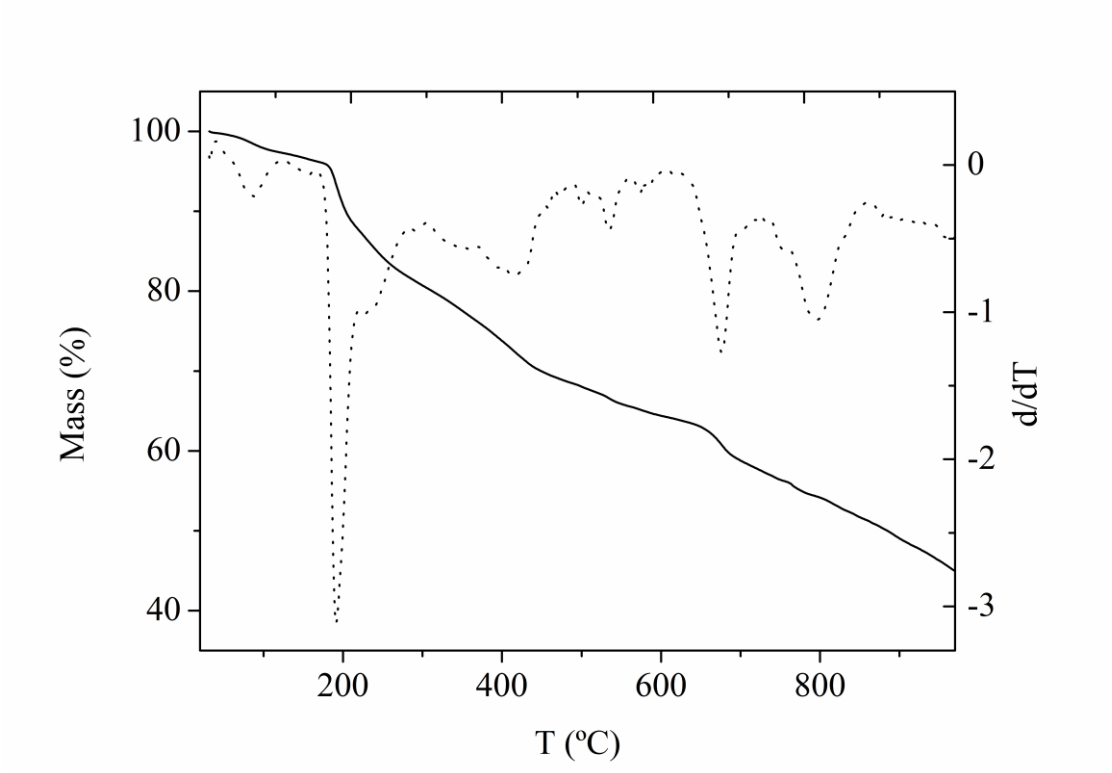


Figure S7a. TGA of $[V^{V}_{2}O_{3}(hop)_{2}(bpy)_{2}]\cdot 7H_{2}O$ (**1**).

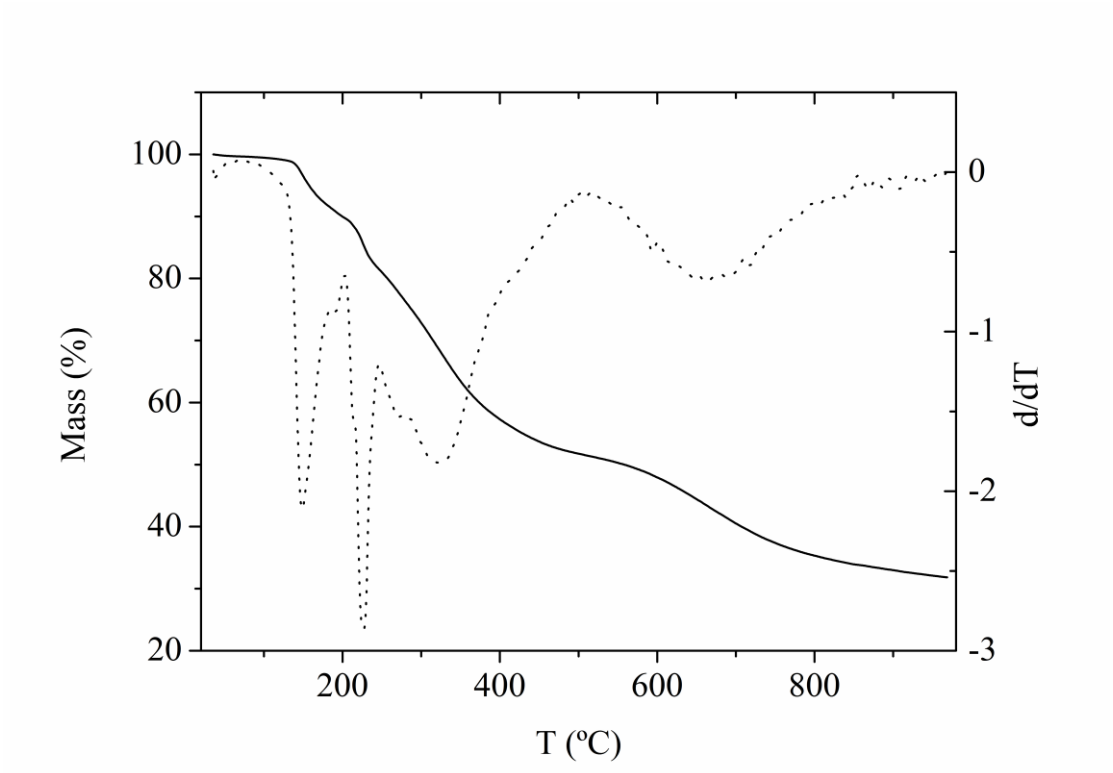


Figure S7b. TGA of $(H_{2}arg)_{n}(V^{V}O_{3})_{n}$ ½n$H_{2}O$ (**4**).

Table S1. Average bond distance (Å) in some common organic groups.

Bond type	Group type	Distance	Bond type	Group type	Distance
C−C		1.53	C−N		1.47−1.50
	C−C(=C)	1.51	C=N		1.34−1.38
	C−C(≡C)	1.47	C−O(H)		1.41−1.44
C=C		1.32		carboxylate/ester	1.30
	conjugated	1.38	C=O		1.19−1.23
				carboxylate	1.21−1.23

Ref: CRC handbook of Chemistry and Physics, 2014–2015, 95th ed.

Table S2. All bond distances (Å) of α-hydroxycarboxylates in **1** ~ **3**.

Selected bond	Distance	Type	Selected bond	Distance	Type
1					
O(4)−C(1)	1.275(4)	C−O	O(3)−C(2)	1.406(3)	C−O
O(6)−C(5)	1.217(4)	C=O	C(2)−C(1)	1.535(4)	C−C
O(5)−C(1)	1.239(4)	C=O	C(2)−C(3)	1.540(5)	C−C
N(1)−C(2)	1.444(4)	N−C	C(5)−C(4)	1.489(5)	C−C
N(1)−C(5)	1.345(4)	N−C	C(4)−C(3)	1.527(5)	C−C
2					
O(3)−C(1)	1.308(7)	C−O	C(4)−C(5)	1.378(7)	C=C
O(4)−C(1)	1.229(7)	C=O	C(2)−C(3)	1.338(8)	C=C
O(2)−C(2)	1.331(6)	C−O	N(1)−C(6)	1.300(7)	C=N
N(2)−C(4)	1.364(7)	C−N	C(3)−C(4)	1.453(7)	C−C
N(2)−C(6)	1.313(7)	C−N	C(1)−C(2)	1.503(7)	C−C
N(1)−C(5)	1.375(6)	C−N			
3					
O(4)−C(1)	1.241(3)	C=O	N(1)−C(6)	1.339(3)	C−N
O(3)−C(1)	1.262(3)	C−O	N(1)−C(5)	1.476(3)	C−N
O(2)−C(2)	1.389(3)	C−O	N(1)−C(2)	1.480(3)	C−N
N(2)−C(6)	1.319(3)	C=N	C(5)−C(4)	1.514(4)	C−C
N(3)−C(6)	1.329(3)	C−N	C(4)−C(3)	1.526(4)	C−C
C(3)−C(2)	1.537(3)	C−C	C(2)−C(1)	1.545(3)	C−C

Table S3. Crystal data summaries of intensity data collections and structural refinements for $[V^{V}_2O_3(hop)_2(bpy)_2]\cdot 7H_2O$ (**1**), $[V^{IV}_2O_2(imha)_2(bpy)_2]\cdot bpy$ (**2**), $(CN_3H_6)[V^{V}O_2(Haimhp)_2]\cdot 2H_2O$ (**3**) and $(H_2arg)_n(V^{V}O_3)_n$ ½nH_2O (**4**).

	$[V^{V}_2O_3(hop)_2(bpy)_2]\cdot 7H_2O$ (**1**)	$[V^{IV}_2O_2(imha)_2(bpy)_2]\cdot bpy$ (**2**)	$(CN_3H_6)[V^{V}O_2(Haimhp)_2]\cdot 2H_2O$ (**3**)	$(H_2arg)_n(V^{V}O_3)_n$ ½nH_2O (**4**)
Empirical formula	$C_{30}H_{40}N_6O_{18}V_2$	$C_{52}H_{24}N_{12}O_8V_2$	$C_{13}H_{30}N_9O_{10}V$	$C_6H_{16}N_4O_{5.5}V$
Formula weight	874.49	1046.71	523.40	283.17
Temperature, K	100.0(1)	100.0(1)	100.0(1)	100.0(1)
Wavelength, Å	1.54184	1.54184	1.54184	1.54184
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*I* 2/*a*	*C* 2/*c*	*C* 2/*c*	*I* 2
Unit cell dimensions				
a, Å	18.1010(3)	21.4251(6)	12.6935(3)	13.8138(6)
b, Å	15.3035(3)	15.6225(4)	10.8889(2)	5.1262(2)
c, Å	15.3035(3)	13.7562(3)	17.1563(4)	17.0635(7)
α, °	90	90	90	90
β, °	103.274(2)	96.682(2)	112.342(3)	112.374(5)
γ, °	90	90	90	90
V, Å^3	3944.15(1)	4573.1(2)	2193.30(9)	1117.34(9)
Z	4	4	4	4
D (calculated), g/cm^3	1.351	1.520	1.585	1.683
Abs. coeff., mm^{-1}	4.565	4.041	4.429	7.666
F(000)	1648.0	2120.0	1096.0	588.0
Crystal size, mm	0.05 ×0.04 ×0.03	0.1 ×0.08 ×0.08	0.2 ×0.1 ×0.05	0.3 ×0.2 ×0.2
2θ range for data collection, °	7.69 ~ 136.49	7.02 ~ 156.49	11.044 ~ 134.634	7.05 ~ 153.32
Reflections collected	10637	8315	5503	5492
Independent reflections	3605	8315	1897	2230
R_{int}	0.0236	0.0623	0.0251	0.0360
Data / restraints /	3605/0/242	8315/165/396	1897/0/159	2230/1/156

parameters				
GOF on F^2	1.070	1.102	1.084	1.097
Final R indices R_1 [$I > 2\sigma(I)$]	0.0475	0.0872	0.0398	0.0410
R_2 [$I > 2\sigma(I)$]	0.1243	0.2574	0.1126	0.1114
Largest diff. peak and hole,e◌Å^{-3}	0.97/-0.38	0.67/-0.65	0.44/-0.42	0.69/-0.48

Table S4. Selected H bond distances (Å) and angles (°) in $[V^{V}_2O_3(hop)_2(bpy)_2]\cdot 7H_2O$ (**1**).

D–H ··A	D–H()	H ··A(Å)	D ··A(Å)	D–H ··A(°)
N_1–H_1 ··O_{1Wa}	0.88(3)	2.26(3)	2.939(4)	133(2)
O_{2W}–H_{2W} ··O_3	0.85	1.96	2.806(3)	172
O_{1W}–H_{1WB} ··O_1	0.85	1.89	2.741(4)	174

Symmetric transformations: (a) *x*, 3/2 − *y*, -½ + *z*. Abbreviation: D, donor atom; H, hydrogen atom; A, acceptor atom.

Table S5. Selected H bond distances (Å) and angles (°) in $[V^{IV}_2O_2(imha)_2(bpy)_2]\cdot bpy$ (**2**).

D–H ··A	D–H()	H ··A(Å)	D ··A(Å)	D–H ··A(°)
N_2–H_2 ··O_{1a}	0.86	1.99	2.843(7)	169
N_2–H_2 ··O_{3a}	0.86	2.60	3.058(6)	115

Symmetric transformations: (a) 3/2 − *x*, -1/2 + *y*, 3/2 − *z*. Abbreviation: D, donor atom; H, hydrogen atom; A, acceptor atom.

Table S6. Selected H bond distances (Å) and angles (°) in $(CN_3H_6)[V^VO_2(Haimhp)_2]\cdot 2H_2O$ (**3**).

D–H ··A	D–H(Å)	H ··A(Å)	D ··A(Å)	D–H ··A(°)
O_{1W}–H_{1WA} ··O_{4a}	0.90(5)	2.19(5)	2.839(3)	129(4)
O_{1W}–H_{1WB} ··O_2	0.97(5)	1.72(5)	2.668(3)	162(4)
N_2–H_{2A} ··O_{1b}	0.86	2.51	3.167(3)	134
N_2–H_{2A} ··O_{1Wc}	0.86	2.28	2.991(3)	140
N_2–H_{2B} ··O_2	0.86	2.38	2.925(3)	121
N_2–H_{2B} ··O_{3d}	0.86	1.95	2.754(3)	154
N_3–H_{3A} ··O_{1b}	0.86	2.09	2.840(3)	145
N_3–H_{3B} ··O_{4e}	0.86	2	2.763(3)	147
N_4–H_{4C} ··O_{1Wf}	0.86	2.06	2.850(3)	153
N_4–H_{4D} ··O_1	0.86	1.95	2.810(3)	176
N_5–H_{5C} ··O_{4g}	0.86	2.58	3.222(3)	132
N_5–H_{5C} ··O_{1Wf}	0.86	2.28	3.016(3)	143
N_5–H_{5D} ··O_{4h}	0.86	2.58	3.222(3)	132
N_5–H_{5D} ··O_{1Wi}	0.86	2.28	3.016(3)	143

Symmetric transformations: (a) ½ + *x*, -½ + *y*, *z*; (b) ½ + *x*, ½ + *y*, *z*; (c) 3/2 − *x*, ½ + *y*, ½ − *z*; (d) 1 − *x*, *y*, ½ − *z*; (e) 3/2 − *x*, 3/2 − *y*, 1 − *z*; (f) -½ + *x*, -½ + *y*, *z;* (g) *x*, -1 + *y*, *z;* (h) 1 − *x*, -1 + *y*, ½ − *z;* (i) 3/2 − *x*, -½ + *y*, ½ − *z.* Abbreviation: D, donor atom; H, hydrogen atom; A, acceptor atom.

Table S7. Selected H bond distances (Å) and angles (°) in $(H_2arg)_n(V^VO_3)_n$ ½nH_2O (**4**).

D–H ··A	D–H(Å)	H ··A(Å)	D ··A(Å)	D–H ··A(°)
N_1–H_{1A} ··O_1	0.89	1.87	2.760(7)	174
N_1–H_{1B} ··O_{5a}	0.89	1.9	2.778(7)	167
N_1–H_{1C} ··O_{4b}	0.89	1.95	2.791(6)	157
O_{1w}–H_{1w} ··O_{3c}	0.85	2	2.848(6)	172
N_2–H_2 ··O_{5d}	0.86	2.03	2.870(8)	166
N_3–H_{3A} ··O_{4d}	0.87	2.5	2.918(7)	110
N_3–H_{3B} ··O_{2e}	0.87	2.43	3.259(7)	161
N_4–H_{4A} ··O_{1w}	0.86	2.06	2.866(7)	156
N_4–H_{4B} ··O_{3f}	0.86	2.09	2.891(7)	154

Symmetric transformations: (a) *x*, -1 + *y*, *z*; (b) 1 − *x*, *y*, 2 − *z*; (c) *x*,1 + *y*, *z*; (d) ½ − *x*, -½ + *y*, 3/2 − *z*; (e) -½ + *x*, -½ + *y*, -½ + *z*; (f) 1 − *x*, *y*, 1 − *z*. Abbreviation: D, donor atom; H, hydrogen atom; A, acceptor atom.

Table S8. Selected bond distances (Å) and angles (°) for $[V^{V}_{2}O_{3}(hop)_{2}(bpy)_{2}]\cdot 7H_{2}O$ (**1**).

1			
V(1)−O(1)	1.627(2)	V(1)−O(2)	1.802(5)
V(1)−O(3)	1.904(2)	V(1)−O(4)	2.063(2)
O(2)−V(1a)	1.802(5)	V(1)−N(2)	2.271(2)
V(1)–N(3)	2.152(2)		
O(3)−V(1)−O(4)	79.68(8)	O(2)−V(1)−O(3)	93.69(9)
O(2)−V(1)−O(4)	163.36(7)	O(1)−V(1)−O(3)	105.48(1)
O(1)−V(1)−O(2)	102.43(8)	O(1)−V(1)−O(4)	94.07(1)
V(1a)−O(2)−V(1)	171.83(2)	O(3)−V(1)−N(3)	160.18(8)
O(3)−V(1)−N(2)	90.04(8)	O(2)−V(1)−N(3)	93.50(1)
O(2)−V(1)−N(2)	83.91(7)	O(4)−V(1)−N(3)	88.28(8)
O(4)−V(1)−N(2)	80.87(8)	N(3)−V(1)−N(2)	72.42(8)
O(1)−V(1)−N(3)	90.91(1)	O(1)−V(1)−N(2)	162.63(1)

Symmetric transformations: (a) 3/2 − *x*, + *y*, 1 − *z*.

Table S9. Selected bond distances (Å) and angles (°) for $[V^{IV}_2O_2(imha)_2(bpy)_2]\cdot bpy$ (**2**).

2			
V(1)−O(1)	1.618(4)	V(1)−O(3)	1.995(4)
V(1)−O(2)	1.924(4)	V(1)−N(3)	2.268(5)
V(1)−N(4)	2.152(5)	V(1)−N(1a)	2.107(4)
N(1a)−V(1)	2.107(4)		
O(1)−V(1)−O(3)	98.83(2)	O(2)−V(1)−O(3)	81.15(2)
O(1)−V(1)−O(2)	109.0(2)	O(1)−V(1)−N(3)	163.9(2)
O(1)−V(1)−N(1a)	95.79(2)	O(1)−V(1)−N(4)	91.01(2)
O(3)−V(1)−N(3)	83.12(2)	O(3)−V(1)−N(1a)	164.21(2)
O(3)−V(1)−N(4)	92.99(2)	N(4)−V(1)−N(3)	72.88(2)
O(2)−V(1)−N(3)	87.09(2)	O(2)−V(1)−N(1a)	88.49(2)
O(2)−V(1)−N(4)	159.71(2)	N(1a)−V(1)−N(3)	84.49(2)
N(1a)−V(1)−N(4)	92.68(2)		

Symmetric transformations: (a) $3/2 - x, 1/2 - y, 2 - z$.

Table S10. Selected bond distances (Å) and angles (°) for $(CN_3H_6)[V^VO_2(Haimhp)_2]\cdot 2H_2O$ (**3**).

3			
V(1)−O(3)	2.182(2)	V(1)−O(2)	1.958(2)
V(1)−O(3a)	2.182(2)	V(1)−O(1)	1.645(2)
V(1)−O(2a)	1.958(2)	V(1)−O(1a)	1.645(2)
O(3a)−V(1)−O(3)	76.97(1)	O(2)−V(1)−O(3)	75.44(7)
O(2)−V(1)−O(3a)	83.53(7)	O(2a)−V(1)−O(3a)	75.44(7)
O(2a)−V(1)−O(3)	83.52(7)	O(2a)−V(1)−O(2)	153.10(1)
O(1a)−V(1)−O(3a)	89.61(8)	O(1)−V(1)−O(3)	89.61(8)
O(1)−V(1)−O(3a)	163.64(8)	O(1a)−V(1)−O(3)	163.64(8)
O(1a)−V(1)−O(2)	93.99(8)	O(1)−V(1)−O(2)	102.33(8)
O(1)−V(1)−O(2a)	93.99(8)	O(1a)−V(1)−O(2a)	102.33(8)
O(1)−V(1)−O(1a)	105.02(1)	C(1)−O(3)−V(1)	117.23(2)
C(2)−O(2)−V(1)	121.04(1)		

Symmetric transformations: (a) $1 - x, + y, ½ - z$.

Table S11. Selected bond distances (Å) and angles ( ) for $(H_2arg)_n(V^VO_3)_n$ ½nH_2O (**4**).

4			
V(1)−O(1)	1.643(4)	V(1)−O(2)	1.795(5)
V(1)−O(2a)	1.803(5)	V(1)−O(3)	1.641(5)
O(2)−V(1b)	1.803(4)		
O(1)−V(1)−O(2a)	111.7(2)	O(3)−V(1)−O(2)	110.6(2)
O(1)−V(1)−O(2)	109.0(2)	O(3)−V(1)−O(2a)	106.7(2)
O(3)−V(1)−O(1)	109.2(2)	V(1)−O(2)−V(1b)	131.7(3)
O(2)−V(1)−O(2a)	109.55(1)		

Symmetric transformations: (a) 3/2 − *x*, -½ + *y*, 3/2 − *z*; (b) 3/2 − *x*, ½ + *y*, 3/2 − *z*.

Table S12. Bond valence calculations for **1** ~ **4**.

Complexes	Atom	N	$\sum S_{ij}$	Δ
$[V^{V}_2O_3(hop)_2(bpy)_2]\cdot 7H_2O$ (**1**)	V(1,2)	+5	4.684	−0.316
$[V^{IV}_2O_2(imha)_2(bpy)_2]\cdot bpy$ (**2**)	V(1,2)	+4	4.169	+0.169
$(CN_3H_6)[V^{V}O_2(Haimhp)_2]\cdot 2H_2O$ (**3**)	V(1)	+5	5.099	+0.099
$(H_2arg)_n(V^{V}O_3)_n$ ½nH_2O (**4**)	V(1)	+5	5.117	+0.117

Table S13. Spectral data of solid-state ^{13}C NMR (in ppm) for $[V^{V}_2O_3(hop)_2(bpy)_2]\cdot 7H_2O$ (**1**), pure L-arginine and $(H_2arg)_n(V^{V}O_3)_n$ ½nH_2O (**4**).

Compounds	**C**ONH	**C**OO	HO**C**NH	**C**H_2	**C**H_2	
1	177.21	173.47	53.89	29.02	26.26	
	COO	HN**C**$^{\varepsilon}$NH_2	H_2N**C**$^{\alpha}$H	NH**C**$^{\delta}H_2$	**C**$^{\beta}H_2$	**C**$^{\gamma}H_2$
L-arginine	181.88	158.40	55.65	42.65	31.44	24.07
4	176.50	157.61	56.76	43.82	30.37	26.43

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