Supporting Information

Iso- and hetero- polyoxovanadium glycolates $[V^{IV}_6O_6(glyc)_6M^{III}(OH)_6]^{3-}$ (M = V, Cr, Fe, Al) encapsulating metal hydroxides

Wan-Ting Jin[a]*, Zhen-Lang Xie[c], Xing Su[a], Chuan-Hua Gao[a], Jing Hu[a], Zhao-Hui Zhou[b]*

[a]*College of Chemical and Material Engineering, Quzhou University, Quzhou, 324000,China, 39091@qzu.edu.cn*

[b]*State Key Laboratory for Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China, zhzhou@xmu.edu.cn*

[c] *College of Food Science and Engineering, Guangdong Ocean University, Yangjiang 529500, China*

Figures and Table Options

Figure S9. Experimental and simulated XRD patterns of polycrystalline sample of $(NH_4)_3[V_6O_6(glyc)_6V(\mu\text{-}OH)_6]\cdot 10H_2O$ (**1**).

Table S1. Crystallographic data for $(NH_4)_3[V_6O_6(glyc)_6V(\mu\text{-}OH)_6]\cdot 10H_2O$(**1**), $(NH_4)_3[V_6O_6(glyc)_6Cr(\mu\text{-}OH)_6][(NH_4)_2SO_4]_2\cdot 6H_2O$ (**2**), $(NH_4)_3[V_6O_6(glyc)_6Fe(\mu\text{-}OH)_6][(NH_4)_2SO_4]_2\cdot 7H_2O$ (**3**) and $(NH_4)_3[V_6O_6(glyc)_6Al(\mu\text{-}OH)_6][(NH_4)_2SO_4]_2\cdot 6H_2O$(**4**).

Table S2. Selected bond distances (Å) and angles (º)for $(NH_4)_3[V_6O_6(glyc)_6V(\mu\text{-}OH)_6]\cdot 10H_2O$(**1**).

Table S3. Selected bond distances (Å) and angles (º) for $(NH_4)_3[V_6O_6(glyc)_6Cr(\mu\text{-}OH)_6][(NH_4)_2SO_4]_2\cdot 6H_2O$ (**2**).

Table S4. Selected bond distances (Å) and angles (º) for $(NH_4)_3[V_6O_6(glyc)_6Fe(\mu\text{-}OH)_6][(NH_4)_2SO_4]_2\cdot 7H_2O$ (**3**).

Table S5. Selected bond distances (Å) and angles (º) for $(NH_4)_3[V_6O_6(glyc)_6Al(\mu\text{-}OH)_6][(NH_4)_2SO_4]_2\cdot 6H_2O$ (**4**).

Table S6. The bond valence analyses of vanadyl glycolate **1** to **4**.

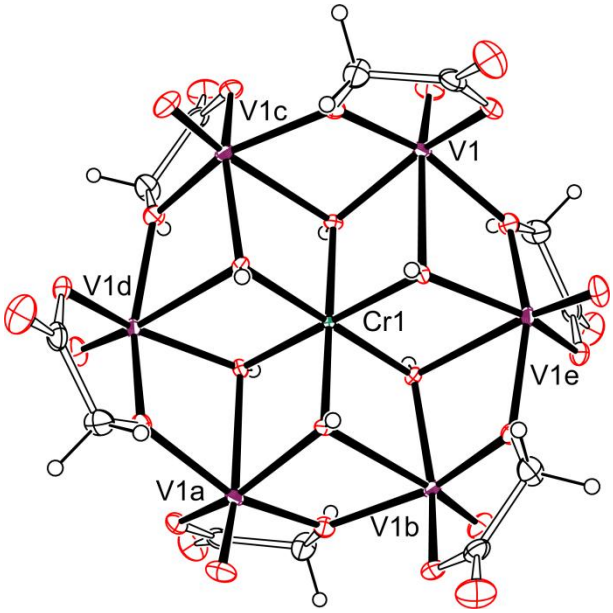

Figure S1. The ORTEP plot of the anion in $(NH_4)_3[V_6O_6(glyc)_6Cr(\mu\text{-}OH)_6][(NH_4)_2SO_4]_2\cdot 6H_2O$ (**2**) at the 30% probability levels.

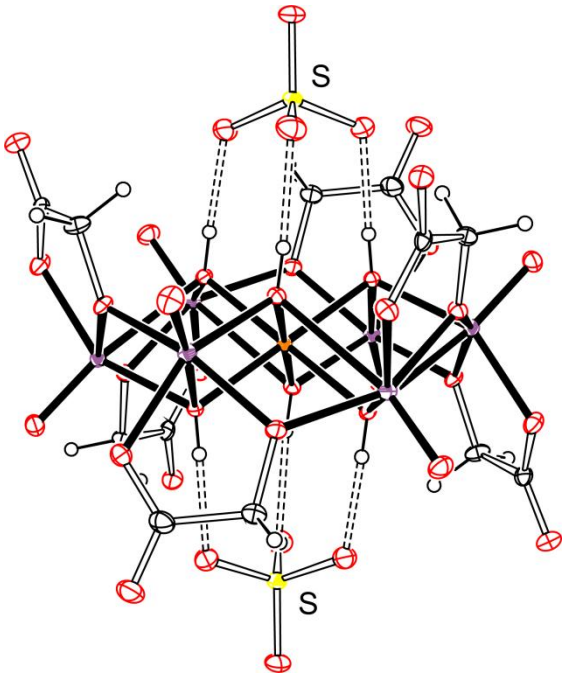

Figure S2. The ORTEP plot of the anion in $(NH_4)_3[V_6O_6(glyc)_6Fe(\mu\text{-}OH)_6][(NH_4)_2SO_4]_2\cdot 6H_2O$ (**3**) at the 30% probability levels.

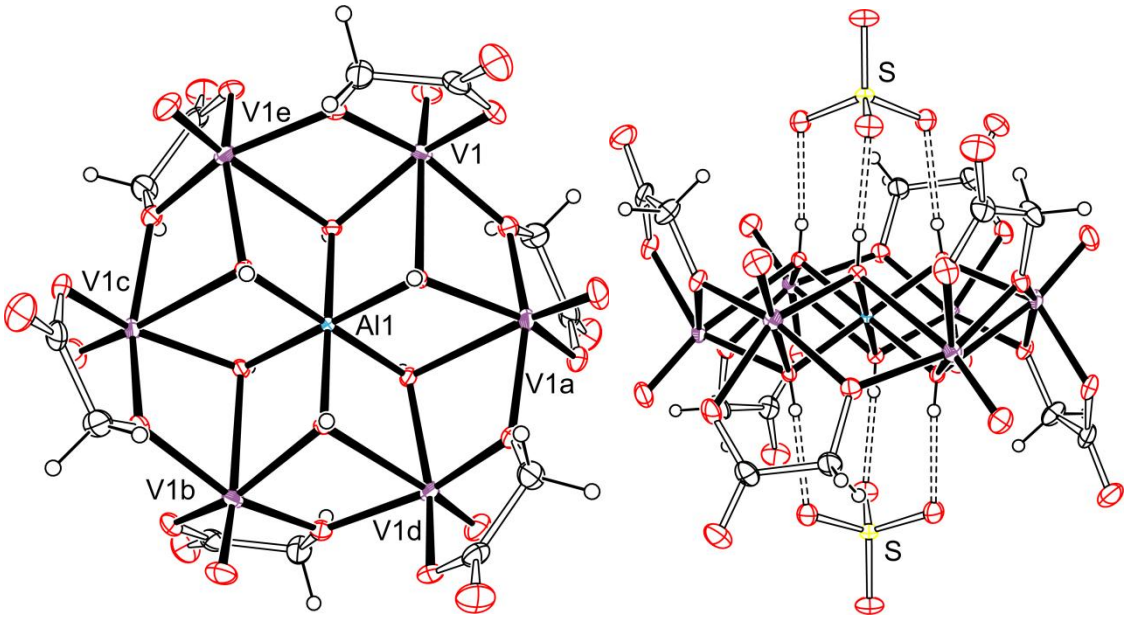

Figure S3. The ORTEP plot of the anion in $(NH_4)_3[V_6O_6(glyc)_6Al(\mu\text{-}OH)_6][(NH_4)_2SO_4]_2\cdot 6H_2O$ (**4**) at the 30% probability levels.

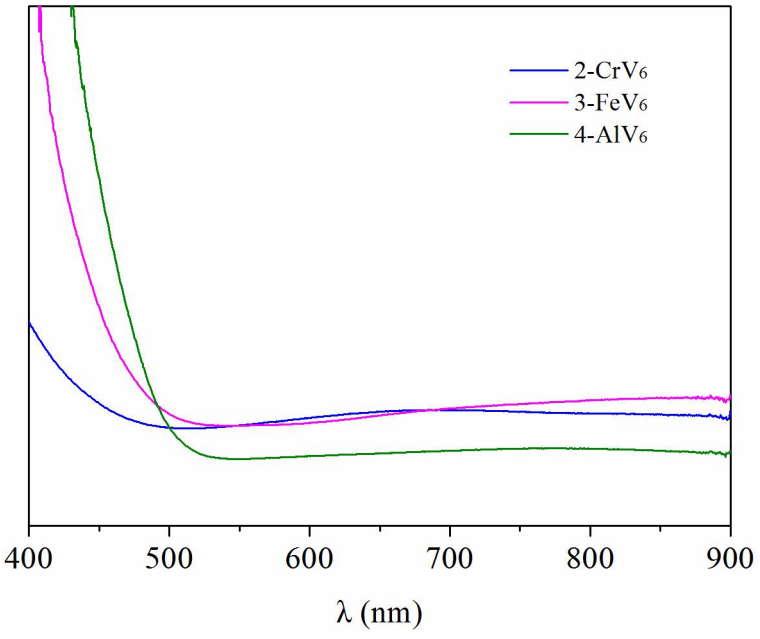

Figure S4. UV-Vis spectra of $(NH_4)_3[V_6O_6(glyc)_6Cr(\mu\text{-}OH)_6][(NH_4)_2SO_4]_2\cdot 6H_2O$ (**2-CrV$_6$**), $(NH_4)_3[V_6O_6(glyc)_6Fe(\mu\text{-}OH)_6][(NH_4)_2SO_4]_2\cdot 7H_2O$ (**3-FeV$_6$**) and $(NH_4)_3[V_6O_6(glyc)_6Al(\mu\text{-}OH)_6][(NH_4)_2SO_4]_2\cdot 6H_2O$ (**4-AlV$_6$**) in dilute solutions standing at room temperature after 5 days.

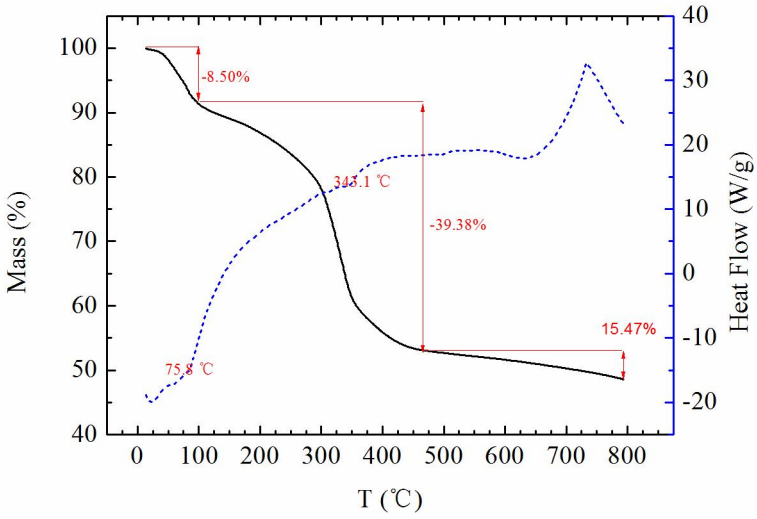

Figure S5. TGA curves of polycrystalline sample of $(NH_4)_3[V_6O_6(glyc)_6V(\mu\text{-}OH)_6]\cdot 10H_2O$(**1-V$_7$**).

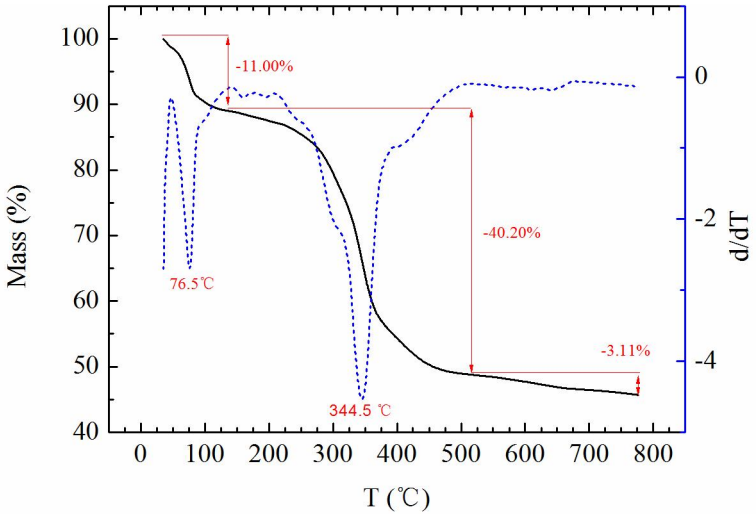

Figure S6. TGA curves of polycrystalline sample of $(NH_4)_3[V_6O_6(glyc)_6Cr(\mu\text{-}OH)_6][(NH_4)_2SO_4]_2\cdot 6H_2O$ (**2-CrV$_6$**).

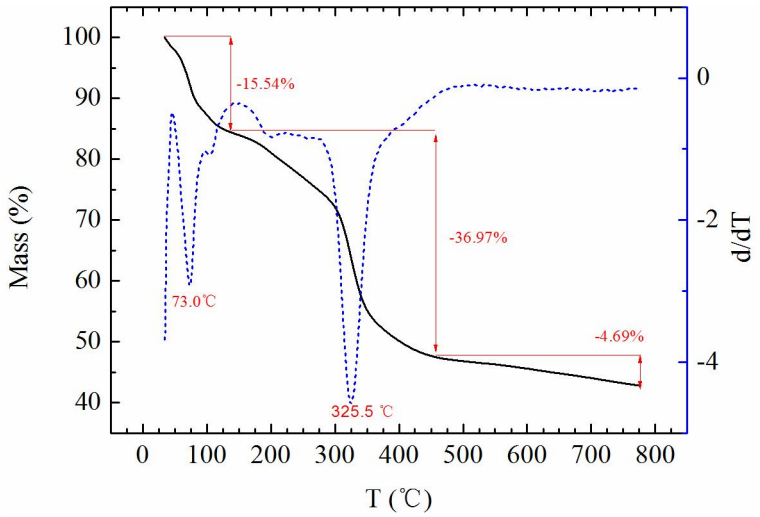

Figure S7. TGA curves of polycrystalline sample of $(NH_4)_3[V_6O_6(glyc)_6Fe(\mu\text{-}OH)_6][(NH_4)_2SO_4]_2\cdot 7H_2O$ (**3-FeV$_6$**).

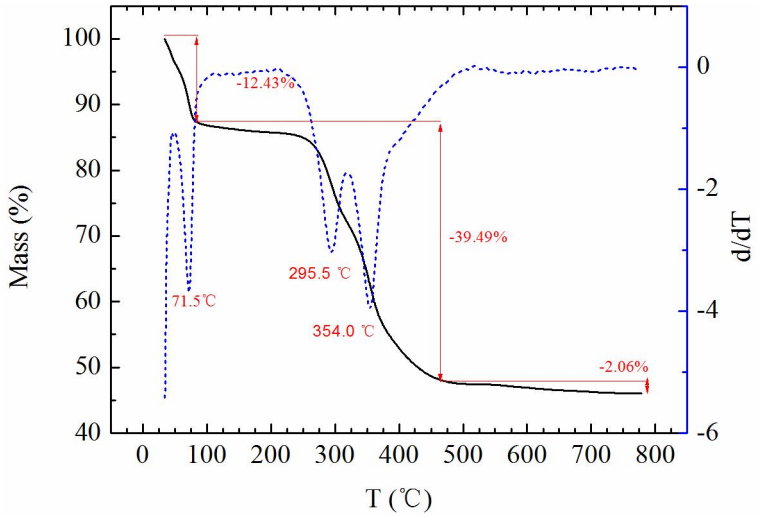

Figure S8. TGA curves of polycrystalline sample of $(NH_4)_3[V_6O_6(glyc)_6Al(\mu\text{-}OH)_6][(NH_4)_2SO_4]_2\cdot 6H_2O$ (**4-AlV$_6$**).

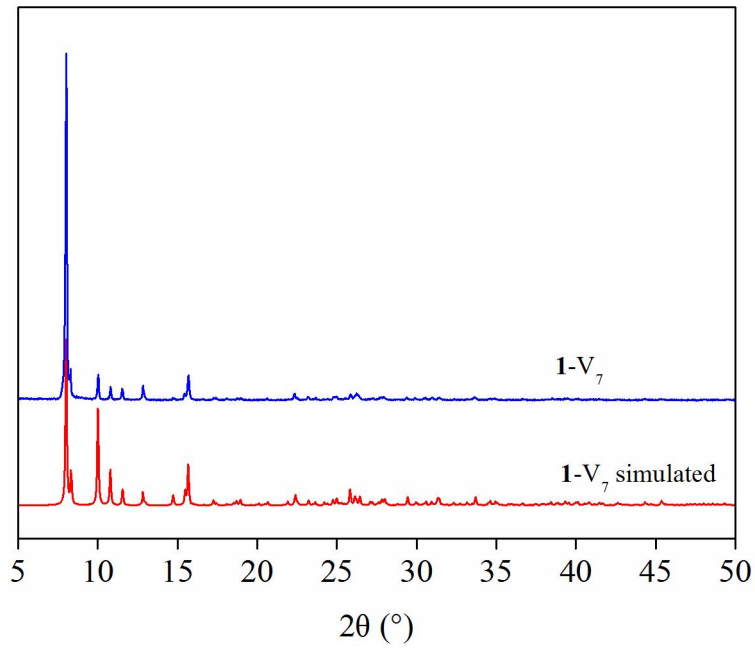

Figure S9. Experimental and simulated XRD patterns of polycrystalline sample of $(NH_4)_3[V_6O_6(glyc)_6V(\mu\text{-}OH)_6]\cdot 10H_2O$(**1**).

Table S1. Crystallographic data for $(NH_4)_3[V_6O_6(glyc)_6V(\mu\text{-}OH)_6]\cdot 10H_2O$(**1**), $(NH_4)_3[V_6O_6(glyc)_6Cr(\mu\text{-}OH)_6][(NH_4)_2SO_4]_2\cdot 6H_2O$ (**2**), $(NH_4)_3[V_6O_6(glyc)_6Fe(\mu\text{-}OH)_6][(NH_4)_2SO_4]_2\cdot 7H_2O$ (**3**) and $(NH_4)_3[V_6O_6(glyc)_6Al(\mu\text{-}OH)_6][(NH_4)_2SO_4]_2\cdot 6H_2O$ (**4**).

	1	**2**	**3**	**4**
Empirical formula	$C_{12}H_{50}N_3O_{40}V_7$	$C_{12}H_{58}CrN_7O_{44}S_2V_6$	$C_{12}H_{60}FeN_7O_{45}S_2V_6$	$C_{12}H_{58}AlN_7O_{44}S_2V_6$
Formula weight	1233.13	1426.41	1448.28	1401.39
Temperature, K	223.0	223	195(2)	174(1)
Wavelength	Cu Kα (λ = 1.54184)		Mo Kα (λ = 0.71073)	
Crystal system	orthorhombic	trigonal	monoclinic	trigonal
Space group	*P bcn*	*R* -3	*C* 2/*c*	*R* -3
Unit cell dimensions				
a, Å	21.2465(18)	11.4407(4)	20.7200(5)	11.3926(5)
b, Å	9.7088(5)	11.4407(4)	11.1750(3)	11.3926(5)
c, Å	22.076(1)	31.328(1)	21.0112(4)	31.486(2)
α, °	90	90	90	90
β, °	90	90	93.255(2)	90
γ,°	90	120	90	120
V, Å^3	4553.8(5)	3551.2(3)	4857.2(2)	3539.2(4)
Z	4	3	4	3
D (calculated), g/cm^3	1.799	2.001	1.980	1.973
Abs.coeff., mm^{-1}	12.586	13.343	1.608	1.376
F(000)	2496.0	2175.0	2948.0	2142.0

Crystal size, mm	0.30×0.10×0.02	0.20×0.20×0.20	0.10×0.35×0.35	0.20×0.20×0.10
2θ range for data collection, °	8.01 to 124.634	8.468 to 124.634	5.756 to 57.652	6.622 to 59.586
Reflections collected	8421	3723	10712	6129
Independent reflections	3581	1231	5496	2018
R_{int}	0.0624	0.0358	0.0301	0.0385
Data / restraints / parameters	3581 / 33 / 2938	1231/9/119	5496/47/404	2018/6/119
GOF on F^2	1.164	1.086	1.080	1.064
Final R indices$R_1[I>2\sigma(I)]$	0.0961	0.0428	0.0346	0.0582
$R_2[I>2\sigma(I)]$	0.2678	0.1218	0.0837	0.1529
Largest diff. peak and hole, e⋅Å^{-3}	1.44 / -1.47	0.96/-0.70	0.76/-0.47	1.37/-0.65

Table S2. Selected bond distances (Å) and angles (º) for $(NH_4)_3[V_6O_6(glyc)_6V(\mu\text{-}OH)_6]\cdot 10H_2O$(**1**).

1			
V1–O15	2.000(5)	V3–O14	2.006(5)
V1–O13[a]	2.419(5)	V3–O15[a]	2.466(5)
V1–O5	2.009(6)	V3–O1[a]	2.014(5)
V1–O1	1.942(5)	V3–O9	1.966(5)
V1–O2	1.995(5)	V3–O10	1.990(5)
V1–O4	1.598(5)	V3–O12	1.599(6)
V2–O14	2.428(5)	V4–O14	1.995(5)
V2–O13[a]	2.002(5)	V4–O14[a]	1.995(5)
V2–O5	1.953(5)	V4–O15[a]	1.999(5)
V2–O9	1.993(5)	V4–O15	1.998(5)
V2–O6	1.989(5)	V4–O13	2.011(5)
V2–O8	1.598(6)	V4–O13[a]	2.011(5)
O15–V1–O13[a]	73.6(2)	O9–V3–O10	81.0(2)
O15–V1–O5	96.2(2)	O10–V3–O14	150.4(2)
O5–V1–O13[a]	69.2(2)	O10–V3–O15[a]	83.6(2)
O1–V1–O15	80.8(2)	O10–V3–O1[a]	91.4(2)
O1-V1–O13[a]	85.3(2)	O12–V3–O14	102.4(3)
O1–V1–O5	154.0(2)	O12–V3–O15[a]	165.3(3)
O1–V1–O2	80.7(2)	O12–V3–O1[a]	98.7(3)
O2–V1–O15	152.7(2)	O12–V3–O9	108.1(3)
O2–V1–O13[a]	85.0(2)	O12–V3–O10	104.9(3)
O2–V1–O5	91.7(2)	O14–V4–O14[a]	180
O4–V1–O15	101.5(2)	O14[a]–V4–O15[a]	96.3(2)
O4–V1–O13[a]	165.9(2)	O14–V4–O15[a]	83.7(2)
O4–V1–O5	98.7(2)	O14[a]–V4–O15	83.7(2)
O4–V1–O1	107.3(3)	O14–V4–O15	96.3(2)

O4–V1–O2	103.0(3)	O14[a]–V4–O13[a]	97.1(2)
O13[a]–V2–O14	72.8(2)	O14–V4–O13[a]	82.9(2)
O5–V2–O14	85.1(2)	O14[a]–V4–O13	82.9(2)
O5–V2–O13[a]	79.8(2)	O14–V4–O13	97.1(2)
O5–V2–O9	154.3(2)	O15–V4–O15[a]	180
O5–V2–O6	80.6(2)	O15[a]–V4–O13[a]	96.5(2)
O9–V2–O14	69.6(2)	O15–V4–O13[a]	83.5(2)
O9–V2–O13[a]	96.6(2)	O15[a]–V4–O13	83.5(2)
O6–V2–O14	82.9(2)	O15–V4–O13	96.5(2)
O6–V2–O13[a]	149.8(2)	O131–V4–O13	180.0(1)
O6–V2–O9	91.2(2)	V4–O14–V2	95.0(2)
O8–V2–O14	166.2(2)	V4–O14–V3	110.0(2)
O8–V2–O13[a]	102.7(3)	V3–O14–V2	96.0(2)
O8–V2–O5	107.1(3)	V4–O15–V1	108.9(2)
O8–V2–O9	98.5(3)	V4–O15–V3[a]	93.9(2)
O8–V2–O6	104.9(3)	V1–O15–V3[a]	95.4(2)
O14–V3–O15[a]	72.4(2)	V4–O13–V1[a]	94.0(2)
O14–V3–O1[a]	95.5(2)	V2[a]–O13–V4	109.3(2)
O1[a]–V3–O15[a]	68.7(2)	V2[a]–O13–V1[a]	96.6(2)
O9–V3–O14	79.9(2)	V2–O5–V1	113.4(2)
O9–V3–O15[a]	84.8(2)	V1–O1–V3[a]	113.9(2)
O9–V3–O1[a]	153.1(2)	V3–O9–V2	113.2(2)

Symmetric transformation:[a]1 -*x*,1-*y*,1-*z*.

Table S3. Selected bond distances (Å) and angles (º) for $(NH_4)_3[V_6O_6(glyc)_6Cr(\mu\text{-}OH)_6][(NH_4)_2SO_4]_2\cdot 6H_2O$ (**2**).

2			
Cr1–O5[a]	1.969(3)	V1–O[e]	2.009(3)
Cr1–O5[b]	1.969(3)	V1–O5[b]	2.458(3)
Cr1–O5	1.969(3)	V1–O1	1.952(3)
Cr1–O5[c]	1.969(3)	V1–O1[b]	1.996(3)
Cr1–O5[d]	1.969(3)	V1–O2	1.986(3)
Cr1–O5[e]	1.969(3)	V1–O4	1.593(3)
O5[a]–Cr1–O5[b]	95.8(1)	O1–V1–O5[e]	85.7(1)
O5[c]-Cr1–O5[d]	95.8(1)	O1–V1–O5	81.0(1)
O5[d]–Cr1–O5[e]	95.9(1)	O1[e]–V1–O5	95.1(1)
O5–Cr1–O5[e]	84.2(1)	O1–V1–O1[e]	154.9(1)
O5–Cr1–O5[e]	84.2(1)	O1–V1–O2	80.5(1)
O5[c]–Cr1–O5[e]	95.9(1)	O2–V1–O5	146.7(1)
O5[a]–Cr1–O5[e]	180	O2–V1–O5[e]	79.6(1)
O5[a]–Cr1–O5	95.8(1)	O2–V1–O1[e]	90.2(1)
O5[b]–Cr1–O5[c]	84.2(1)	O4–V1–O5	103.3(1)
O5[b]–Cr1–O5[e]	84.2(1)	O4–V1–O5[e]	165.4(1)
O5–Cr1–O5[c]	180	O4–V1–O1	107.3(2)
O5[b]–Cr1–O5	95.8(1)	O4–V1–O1[e]	97.7(2)
O5[a]–Cr1–O5[d]	84.2(1)	O4–V1–O2	108.5(2)
O5[b]–Cr1–O5[d]	180	Cr1–O5–V1[d]	94.2(1)
O5[a]–Cr1–O5[c]	84.2(1)	Cr1–O5–V1	110.0(1)
O5–V1–O5[e]	71.6(1)	V1–O5–V1[d]	94.7(1)
O1[e]–V1–O5[e]	69.7(1)	V1–O1–V1[d]	113.4(1)

Symmetric transformation:[a] $1 + y - x, 1 - x, +z$; [b] $1 - y, +x - y, +z$; [c] $4/3 - x, \frac{2}{3} - y, \frac{2}{3} - z$; [d] $\frac{1}{3} + y, \frac{2}{3} - x + y, \frac{2}{3} - z$; [e] $\frac{1}{3} - y + x, -\frac{1}{3} + x, \frac{2}{3} - z$

Table S4. Selected bond distances (Å) and angles (º) for $(NH_4)_3[V_6O_6(glyc)_6Fe(\mu\text{-}OH)_6][(NH_4)_2SO_4]_2\cdot 7H_2O$ (**3**).

3			
Fe1–O15	1.999(2)	V2–O5	1.959(2)
Fe1–O14[a]	2.015(2)	V2–O9	1.993(2)
Fe1–O14	2.015(2)	V2–O6	1.996(2)
V1–O4	1.594(2)	V2–O13	2.009(2)
V1–O1	1.9618(2)	V2–O15[a]	2.447(2)
V1–O5	2.006(2)	V3–O12	1.592(2)
V1–O2	2.007(2)	V3–O9	1.954(2)
V1–O14	2.007(2)	V3–O10	1.978(2)
V1–O13	2.464(2)	V3–O1[a]	1.999(2)
V2–O8	1.604(2)	V3–O15[a]	2.004(2)
O13–Fe1–O13[a]	180	O8-V2–O6	105.82(9)
O13–Fe1–O15[a]	83.60(7)	O5–V2–O6	81.29(7)
O13[a]–Fe1–O15[a]	96.40(7)	O9–V2–O6	91.06(7)
O13–Fe1–O15	96.40(7)	O8–V2–O13	103.19(9)
O13[a]–Fe1–O15	83.60(7)	O5–V2–O13	81.14(7)
O15[a]–Fe1–O15	180.00(9)	O9–V2–O13	94.23(7)
O13–Fe1–O14[a]	95.67(7)	O6–V2–O13	149.35(8)
O13[a]–Fe1–O14[a]	84.33(7)	O8–V2–O15[a]	166.79(8)
O15[a]–Fe1–O14[a]	85.96(7)	O5–V2–O15[a]	85.32(6)
O15–Fe1–O14[a]	94.03(7)	O9–V2–O15[a]	69.65(6)
O13–Fe1–O14	84.33(7)	O6–V2–O15[a]	81.04(7)
O13[a]–Fe1–O14	95.67(7)	O13–V2–O15[a]	72.66(6)
O15[a]–Fe1–O14	94.04(7)	O12–V3–O9	109.48(9)
O15–Fe1–O14	85.97(7)	O12–V3–O10	105.88(9)
O14[a]–Fe1–O14	180	O9–V3–O10	81.37(7)
O4–V1–O1	106.67(9)	O12–V3–O1[a]	99.15(9)

O4–V1–O5	99.53(9)	O9–V3–O1[a]	151.33(7)
O1–V1–O5	153.72(7)	O10–V3–O1[a]	89.63(7)
O4–V1–O2	104.68(9)	O12–V3–O15[a]	104.91(9)
O1–V1–O2	80.57(7)	O9–V3–O15[a]	80.69(7)
O5–V1–O2	91.03(8)	O10–V3–O15[a]	148.09(7)
O4–V1–O14	105.60(9)	O1[a]–V3–O15[a]	93.63(7)
O1–V1–O14	81.31(7)	V1–O1–V3[a]	115.81(9)
O5–V1–O14	93.75(7)	V2–O5–V1	113.11(8)
O2–V1–O14	148.07(7)	V3–O9–V2	112.95(8)
O4–V1–O13	168.86(9)	Fe1–O13–V2	109.53(8)
O1–V1–O13	84.24(7)	Fe1–O13–V1	93.64(6)
O5–V1–O13	69.68(6)	V2–O13–V1	94.85(6)
O2–V1–O13	78.93(7)	V1–O14–Fe1	108.71(8)
O14–V1–O13	73.27(6)	Fe1–O15–V3[a]	110.41(8)
O8–V2–O5	106.69(9)	Fe1–O15–V2[a]	94.21(6)
O8–V2–O9	98.58(9)	V3[a]–O15–V2[a]	94.82(7)
O5–V2–O9	154.72(7)		

Symmetric transformation:[a] ½ - *x*, ½ - *y*, 1 - *z*.

Table S5. Selected bond distances (Å) and angles (º) for $(NH_4)_3[V_6O_6(glyc)_6Al(\mu\text{-}OH)_6][(NH_4)_2SO_4]_2\cdot 6H_2O$ (**4**).

4			
V1–O5[a]	2.454(3)	Al1–O5[d]	1.899(2)
V1–O5	2.019(2)	Al1–O5[b]	1.899(2)
V1–O1	1.949(3)	Al1–O5[c]	1.899(2)
V1–O1[a]	1.993(3)	Al1–O5[a]	1.899(2)
V1–O2	1.993(3)	Al1–O5[e]	1.899(2)
V1–O4	1.597(3)	Al1–O5	1.899(2)
O5–V1–O5[a]	69.0(1)	O5[e]–Al1–O5	180.0(1)
O1-V1–O5	81.9(1)	O5[a]–Al1–O5[c]	84.7(1)
O1[a]–V1–O5	94.7(1)	O5[c]–Al1–O5[b]	95.3(1)
O1[a]–V1–O5[a]	70.7(1)	O5[e]–Al1–O5[d]	95.3(1)
O1–V1–O5[a]	85.7(1)	O5[a]–Al1–O5[b]	180
O1–V1–O1[a]	155.6(1)	O5[a]–Al1–O5[d]	95.3(1)
O1–V1–O2	80.7(1)	O5[b]–Al1–O5	95.3(1)
O2–V1–O5[a]	80.6(1)	O5[c]–Al1–O5	95.3(1)
O2–V1–O5	145.9(1)	O5[d]–Al1–O5	84.7(1)
O2–V1–O1[a]	89.3(1)	O5[d]–Al1–O5[c]	180
O4–V1–O5	103.7(1)	O5[e]–Al1–O5[a]	95.3(1)
O4–V1–O5[a]	165.1(1)	O5[e]–Al1–O5[b]	84.7(1)
O4–V1–O1[a]	97.7(1)	O5[e]–Al1–O5[c]	84.7(1)
O4–V1–O1	106.6(2)	V1–O5–V1[d]	93.58(9)
O4–V1–O2	109.3(2)	Al1–O5–V1[d]	95.1(1)
O5[a]–Al1–O5	84.7(1)	Al1–O5–V1	111.2(1)
O5[d]–Al1–O5[b]	84.7(1)	V1–O1–V1[d]	112.3(1)

Symmetric transformations: [a]⅓ + *y*, ⅔ - *x* + *y*, ⅔ - *z*; [b] 1 - *y*, +*x* - *y*, +*z*; [c] 1 + *y* - *x*, 1 - *x*, +*z*; [d]⅓ - *y* + *x*, -⅓ + *x*, ⅔ - *z*; [e] 4/3 - *x*, ⅔ - *y*, ⅔ - *z*

Table S6.The valence analyses of vanadyl glycolate **1** ~ **4**.

Sample	atom	ΣS_{ij}	Δ
$(NH_4)_3[V_6O_6(glyc)_6V(\mu\text{-}OH)_6]\cdot 10H_2O$(**1**)	V(1)	4.147	+0.147
	V(2)	4.159	+0.159
	V(3)	3.921	-0.079
	V(4)	2.985	-0.015
$(NH_4)_3[V_6O_6(glyc)_6Cr(\mu\text{-}OH)_6][(NH_4)_2SO_4]_2\cdot 6H_2O$ (**2**)	V(1)	4.154	+0.154
	Cr(1)	3.093	+0.093
$(NH_4)_3[V_6O_6(glyc)_6Fe(\mu\text{-}OH)_6][(NH_4)_2SO_4]_2\cdot 7H_2O$ (**3**)	V(1)	3.934	-0.066
	V(2)	4.093	+0.093
	V(3)	4.013	+0.013
	Fe(1)	3.098	+0.098
$(NH_4)_3[V_6O_6(glyc)_6Al(\mu\text{-}OH)_6][(NH_4)_2SO_4]_2\cdot 6H_2O$ (**4**)	V(1)	4.133	+0.133
	Al(1)	2.828	-0.172