Supporting information

Asymmetric dinuclear, hexanuclear and octanuclear oxovanadium citrates with triazolates: Novel mixed-ligands and mixed-valence complexes

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$K_2\{[V^{IV/V}{}_2O_2(cit)(Hdatrz)(datrz)]_2[V^{IV}{}_2O_2(cit)(Hdatrz)(datrz)]_2\}\cdot 27.5H_2O$ (**5**), respectively. 12

Table S3. Hydrogen bonds observed in $[V_2O_2(cit)(Hdatrz)_3]\cdot 5H_2O$ (**1**), $[V_2O_2(cit)(Hdatrz)_3][V_2O_2(cit)_2]_{½}\cdot 2H_2datrz\cdot 9.5H_2O$ (**2**), $V_6O_6(\mu_3\text{-}O)_2(cit)_2(Hdatrz)_4]\cdot 4H_2O$ (**3**), $[V_3O_6(\mu_2\text{-}OH)(\mu_3\text{-}O)(Hdatrz)_2]\cdot 4.5H_2O$ (**4**) and $K_2\{[V^{IV/V}{}_2O_2(cit)(Hdatrz)(datrz)]_2[V^{IV}{}_2O_2(cit)(Hdatrz)(datrz)]_2\}\cdot 27.5H_2O$ (**5**), respectively. 17

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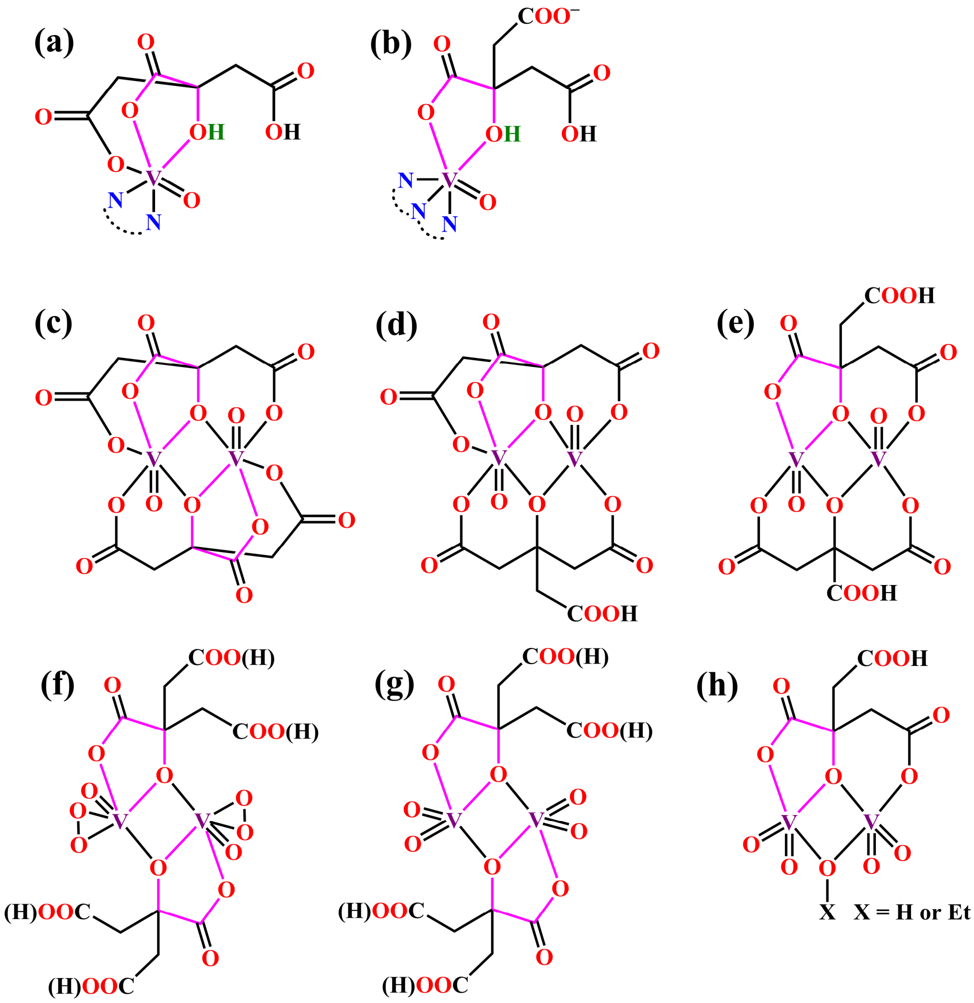

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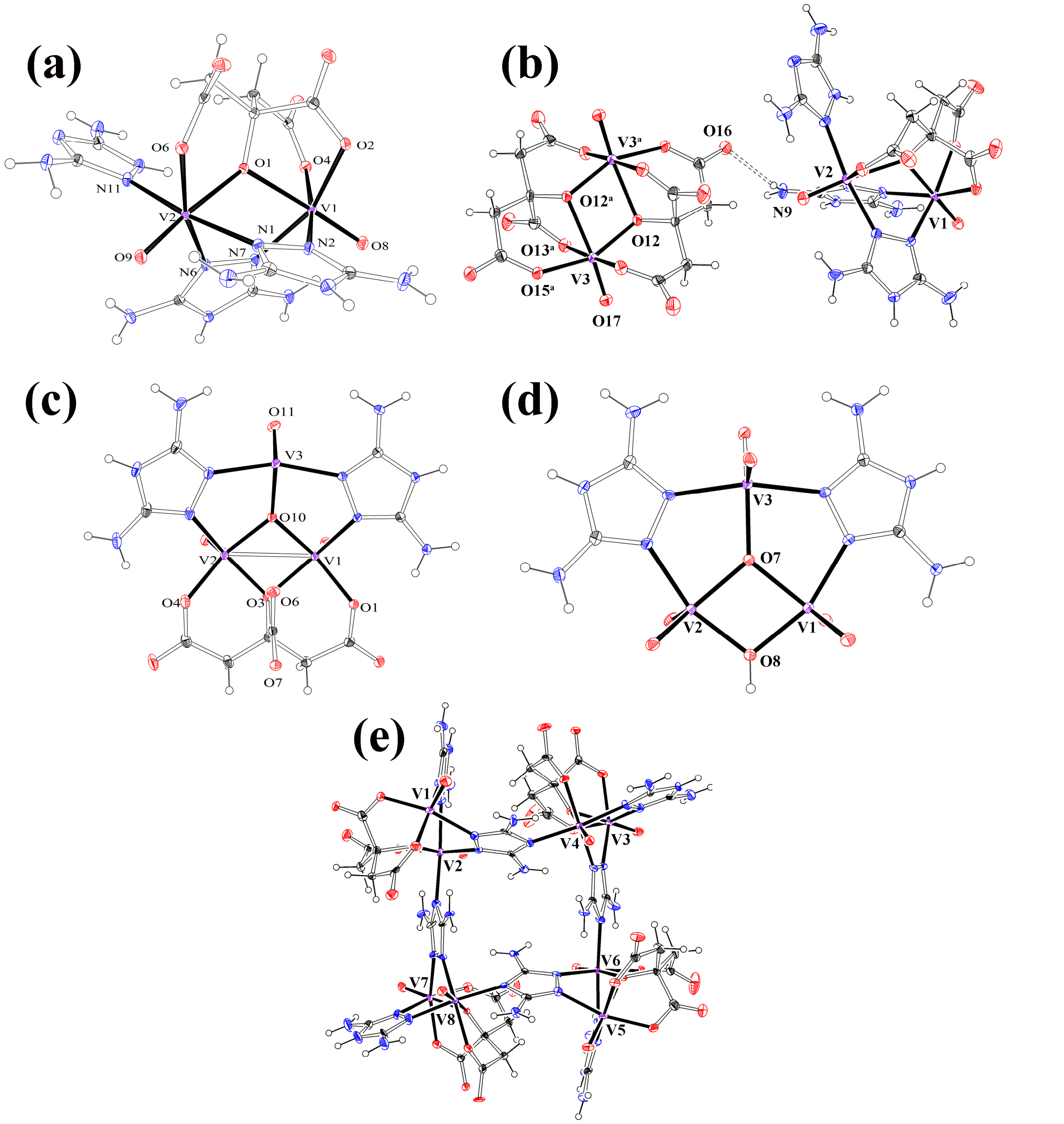

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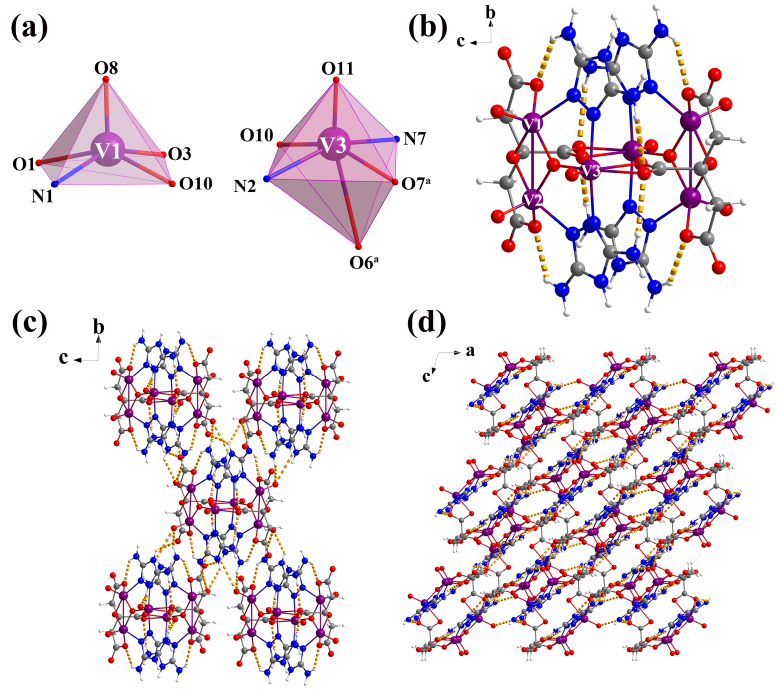

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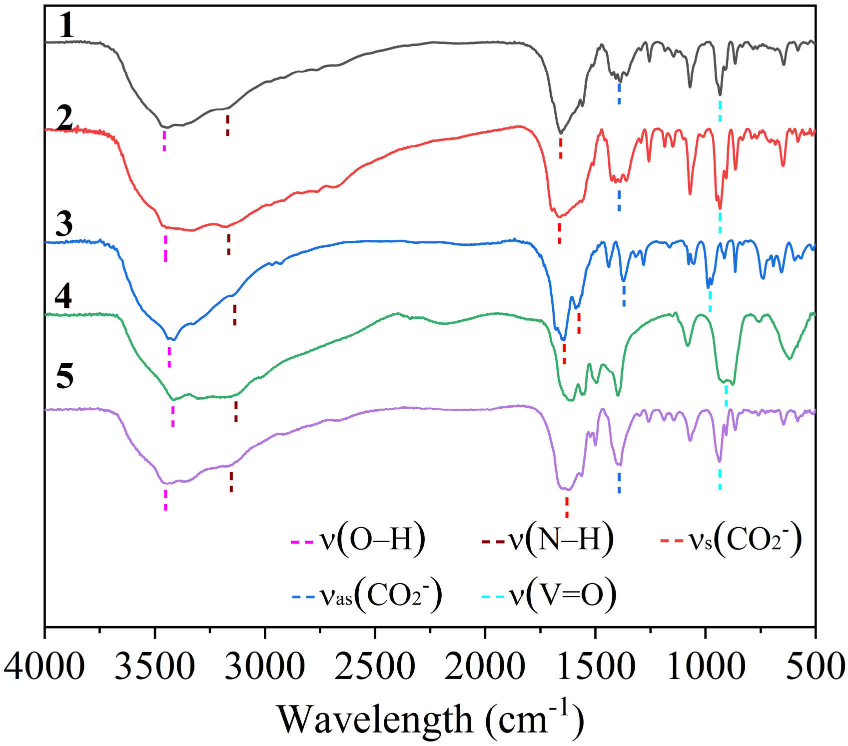

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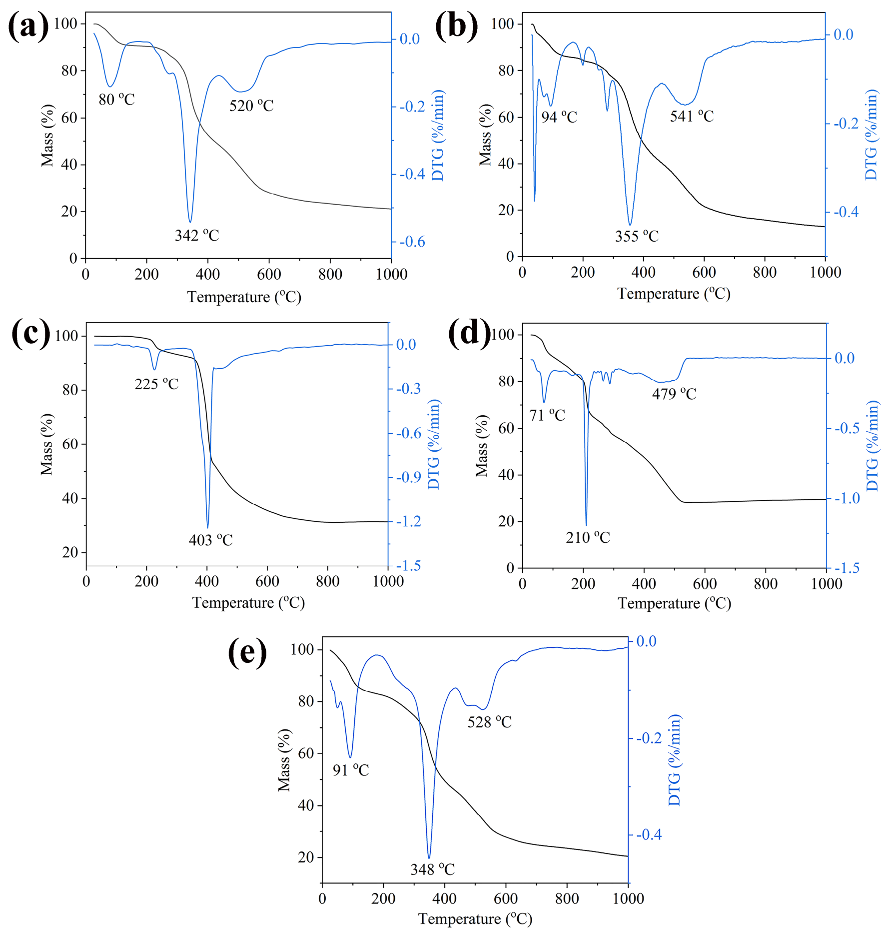
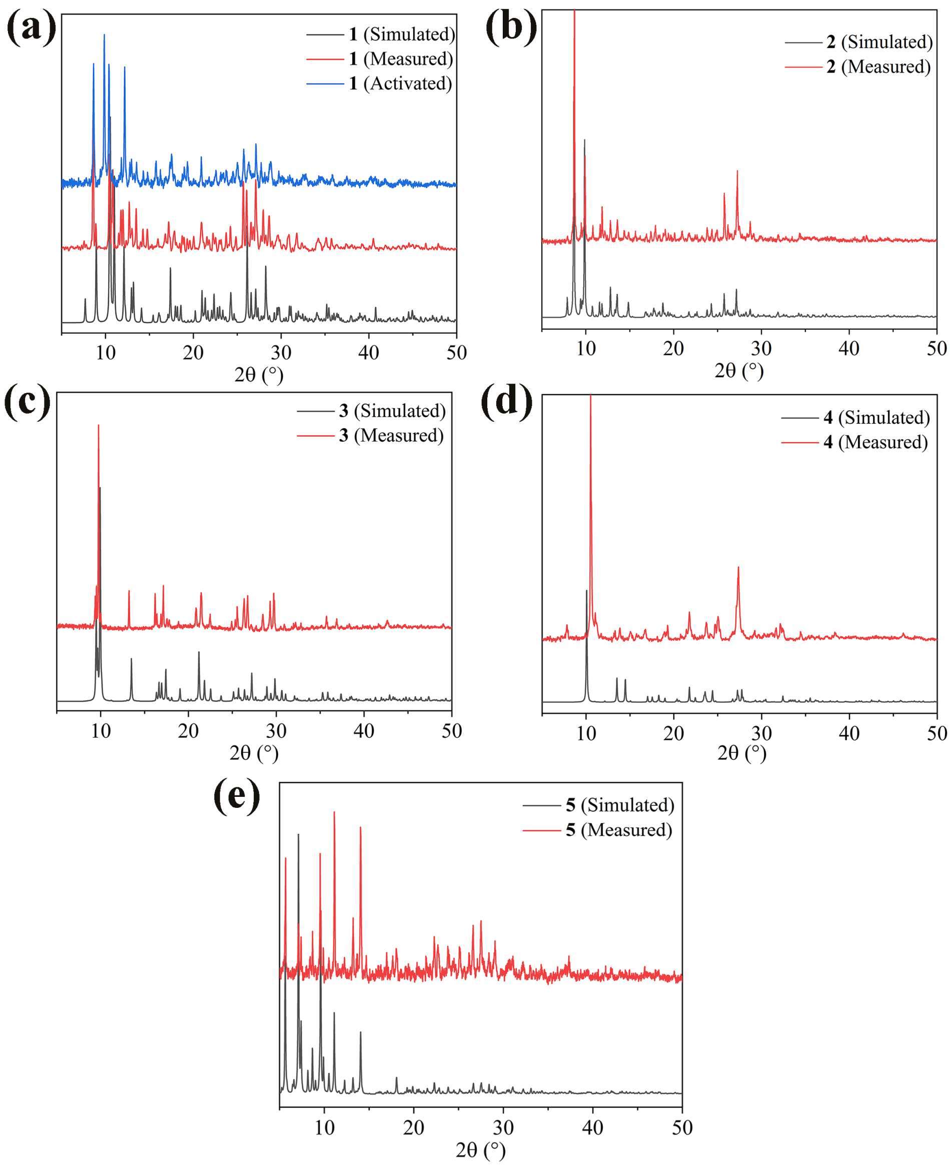


Figure S5. (a – e) TGA curves of **1**–**5** in N_2 stream at a heating rate of 10 °C min^{-1}, respectively.



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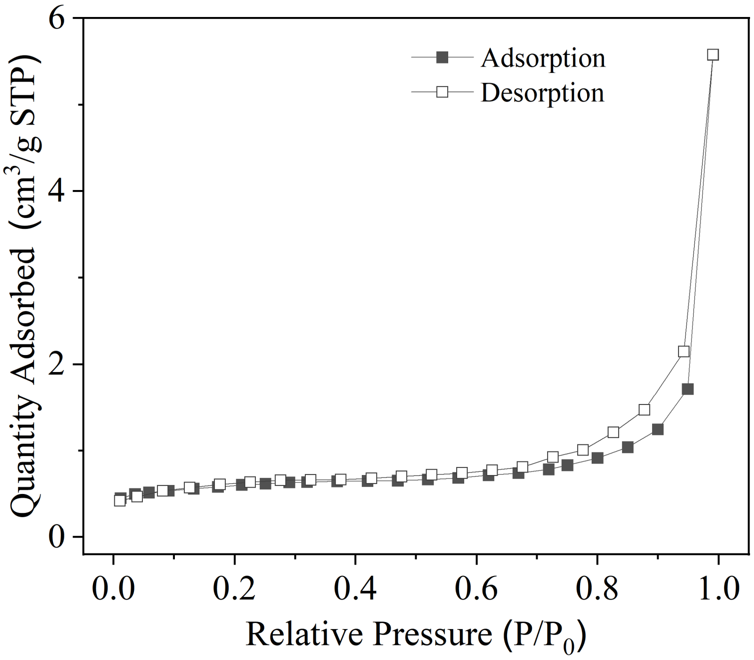

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	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{12}H_{29}N_{15}O_{14}V_2$	$C_{22}H_{53}N_{25}O_{26.5}V_3$	$C_{20}H_{36}N_{20}O_{26}V_6$	$C_4H_{20}N_{10}O_{12.5}V_3$	$C_{40}H_{99}K_2N_{40}O_{63.5}V_8$
Formula weight	709.38	1244.71	1278.33	561.12	2642.31
Temperature/K	100(2)	233(1)	100(1)	100(2)	100(1)
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\ 2_1/c$	$P\ \bar{1}$	$P\ 2_1/n$	$P\ 2_1/n$	$P\ 2_1/n$
a/Å	10.3068(2)	10.4466(4)	10.6045(2)	10.3231(2)	20.3045(2)
b/Å	16.4045(2)	10.7317(4)	18.2772(3)	17.2111(3)	18.4546(2)
c/Å	16.7884(3)	22.64026)	11.2855(2)	10.4223(2)	26.9082(2)
α/°	90	82.025(2)	90	90	90
β/°	106.654(2)	89.802(3)	106.3481(2)	101.788(2)	93.6380(2)
γ/°	90	78.306(3)	90	90	90
Volume/Å^3	2719.48(8)	2460.67(2)	2098.93(7)	1812.70(6)	10062.49(2)
Z	4	2	2	4	4
ρ_{calc}g/cm^3	1.733	1.680	2.023	2.056	1.744
μ/mm^{-1}	6.611	5.681	11.833	13.549	7.819
F(000)	1456.0	1282.0	1284.0	1132.0	5396.0
Crystal size/mm^3	0.20 × 0.15 × 0.15	0.15 × 0.1 × 0.1	0.15 × 0.1 × 0.1	0.15 × 0.10 × 0.10	0.20 × 0.15 × 0.10
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2θ range for data collection/°	7.698 to 148.748	8.330 to 133.978	8.330 to 133.978	10.078 to 150.012	5.294 to 139.46
Reflections collected	17071	16902	13873	10675	71737
Independent reflections	5267	8843	4055	3054	18443

R_{int}	0.0367	0.0507	0.0371	0.0589	0.0428
Data/restraints/parameters	5267/25/430	8843/289/668	4055/0/308	3504/0/235	18443/78/1256
Goodness of fit on F^2	1.049	1.082	1.056	1.072	1.051
Final R indexes [I>=2σ(I)]	R_1 = 0.0326, wR_2 = 0.0845	R_1 = 0.0608, wR_2 = 0.1435	R_1 = 0.0311, wR_2 = 0.0796	R_1 = 0.0537, wR_2 = 0.1505	R_1 = 0.0483, wR_2 = 0.1365
Final R indexes [all data]	R_1 = 0.0360, wR_2 = 0.0866	R_1 = 0.0742, wR_2 = 0.1502	R_1 = 0.0330, wR_2 = 0.0811	R_1 = 0.0568, wR_2 = 0.1536	R_1 = 0.0557, wR_2 = 0.1424
Largest diff. peak and hole / eÅ^{-3}	0.39/-0.41	0.55/-0.47	0.38/-0.40	1.24/-1.31	1.00/-0.67

Table S2. Selected bond distances (Å) and angles (º) for $[V_2O_2(cit)(Hdatrz)_3]\cdot 5H_2O$ (**1**), $[V_2O_2(cit)(Hdatrz)_3][V_2O_2(cit)_2]_{½}\cdot 2H_2datrz\cdot 9.5H_2O$ (**2**), $V_6O_6(\mu_3\text{-}O)_2(cit)_2(Hdatrz)_4]\cdot 4H_2O$ (**3**), $[V_3O_6(\mu_2\text{-}OH)(\mu_3\text{-}O)(Hdatrz)_2]\cdot 4.5H_2O$ (**4**) and $K_2\{[V^{IV/V}{}_2O_2(cit)(Hdatrz)(datrz)]_2[V^{IV}{}_2O_2(cit)(Hdatrz)(datrz)]_2\}\cdot 27.5H_2O$ (**5**), respectively.

1			
V1–O1	2.0803(2)	V2–O1	2.0810(2)
V1–O4	2.0204(2)	V2–O6	2.0184(2)
V1–O2	2.0294(2)	V2–O9	1.6154(2)
V1–O8	1.6202(2)	V2–N1	2.1103(2)
V1–N2	2.0856(2)	V2–N11	2.0919(2)
V1–N7	2.0571(2)	V2–N6	2.0872(2)
O1–V1–N2	84.48(7)	O1–V2–N1	82.48(6)
O4–V1–O1	84.91(6)	O1–V2–N11	88.66(7)
O4–V1–O2	87.18(7)	O1–V2–N6	79.03(6)
O4–V1–N2	169.02(7)	O6–V2–O1	85.56(6)
O4–V1–N7	93.25(7)	O6–V2–N1	87.69(7)
O2–V1–O1	78.16(6)	O6–V2–N11	92.28(7)
O2–V1–N2	87.87(7)	O6–V2–N6	164.51(7)
O2–V1–N7	157.25(7)	O9–V2–O1	175.38(7)
O8–V1–O1	177.88(7)	O9–V2–O6	97.55(7)
O8–V1–O4	96.23(7)	O9–V2–N1	94.20(8)
O8–V1–O2	103.66(7)	O9–V2–N11	94.61(8)
O8–V1–N2	94.46(8)	O9–V2–N6	97.74(8)
O8–V1–N7	98.91(8)	N11–V2–N1	171.12(7)
N7–V1–O1	79.22(6)	N6–V2–N1	88.79(7)
N7–V1–N2	87.55(7)	N6–V2–N11	88.91(7)
2			
V1–O3	2.062(3)	V2–N6	2.081(3)
V1–O6	2.014(3)	V2–N11	2.101(4)
V1–O4	2.019(3)	V2–N1	2.087(4)
V1–O9	1.620(3)	V3–O12[a]	2.188(3)
V1–N7	2.080(3)	V3–O12	1.971(3)
V1–N2	2.080(4)	V3–O10	2.037(3)
V2–O3	2.082(3)	V3–O15[a]	2.033(3)
V2–O1	2.012(3)	V3–O13[a]	2.059(3)
V2–O8	1.608(3)	V3–O17	1.611(3)

O4–V1–N2	88.91(2)	O3–V2–N11	90.65(2)
O9–V1–O3	179.29(2)	O3–V2–N1	81.62(2)
O9–V1–O6	96.19(2)	O1–V2–O3	85.52(2)
O9–V1–O4	101.71(2)	O1–V2–N6	164.69(2)
O9–V1–N7	98.92(2)	O1–V2–N11	91.04(2)
O9–V1–N2	95.33(2)	O1–V2–N1	87.12(2)
N7–V1–N2	86.73(2)	O8–V2–O3	174.65(2)
O3–V1–N7	80.59(2)	O12–V3–O12[a]	74.96(2)
O3–V1–N2	84.13(2)	O12–V3–O10	87.50(2)
O6–V1–O3	84.36(2)	O12–V3–O15[a]	153.61(2)
O6–V1–O4	87.05(2)	O12–V3–O13[a]	92.46(2)
O6–V1–N7	93.20(2)	O10–V3–O12[a]	101.31(2)
O6–V1–N2	168.35(2)	O10–V3–O13[a]	176.52(2)
O4–V1–O3	78.75(2)	O151–V3–O12[a]	80.24(2)
O4–V1–N7	159.22(2)	O151–V3–O10	88.66(2)
O8–V2–O1	96.92(2)	O151–V3–O13[a]	89.84(2)
O8–V2–N6	97.83(2)	O131–V3–O12[a]	75.33(2)
O8–V2–N11	94.06(2)	O17–V3–O12	105.47(2)
O8–V2–N1	93.72(2)	O17–V3–O12[a]	163.86(2)
N6–V2–O3	79.44(2)	O17–V3–O10	94.82(2)
N6–V2–N11	91.98(2)	O17–V3–O15[a]	100.87(2)
N6–V2–N1	87.87(2)	O17–V3–O13[a]	88.55(2)
N1–V2–N11	172.17(2)		

Symmetric codes: (a) $2 - x$, $3 - y$, $-z$

3

V1–V2	2.8560(5)	V3–O11	1.6020(17)
V1–O3	2.0001(16)	V3–N2	2.0621(19)
V1–O1	1.9875(16)	V3–N7	2.075(2)
V1–O10	1.9130(15)	V2–O3	1.9868(16)
V1–O8	1.5960(16)	V2–O10	1.9092(16)
V1–N1	2.0723(18)	V2–O4	1.9936(17)
V3–O10	1.8888(16)	V2–O9	1.6012(17)
V3–O7[a]	2.0632(16)	V2–N6	2.063(2)
V3–O6[a]	2.4330(16)		

O3–V1–V2	44.06(4)	O11–V3–O7[a]	97.97(8)
O3–V1–N1	154.30(7)	O11–V3–O6[a]	155.76(8)
O1–V1–V2	126.88(5)	O11–V3–N2	100.24(9)
O1–V1–O3	89.17(6)	O11–V3–N7	101.93(9)
O1–V1–N1	86.86(7)	N2–V3–O7[a]	91.60(7)
O10–V1–V2	41.60(5)	N2–V3–O6[a]	80.20(7)
O10–V1–O3	85.54(6)	N2–V3–N7	157.54(8)
O10–V1–O1	147.30(7)	N7–V3–O6[a]	81.12(7)

O10–V1–N1	84.21(7)	O3–V2–V1	44.43(4)
O8–V1–V2	109.23(6)	O3–V2–O4	88.56(7)
O8–V1–O3	103.23(8)	O3–V2–N6	155.61(7)
O8–V1–O1	104.29(8)	O10–V2–V1	41.70(5)
O8–V1–O10	108.34(8)	O10–V2–O3	86.01(6)
O8–V1–N1	102.35(8)	O10–V2–O4	149.28(7)
N1–V1–V2	123.12(5)	O10–V2–N6	84.87(7)
O10–V3–O7[a]	153.34(7)	O4–V2–V1	127.46(5)
O10–V3–O6[a]	95.52(6)	O4–V2–N6	87.82(8)
O10–V3–N2	84.51(7)	O9–V2–V1	109.07(7)
O10–V3–N7	84.99(7)	O9–V2–O3	104.07(8)
O71–V3–O6[a]	57.86(6)	O9–V2–O10	107.21(8)
O71–V3–N7	88.94(7)	O9–V2–O4	103.45(8)
O11–V3–O10	108.68(8)	O9–V2–N6	100.23(8)

Symmetric codes: (a) $1 - x$, $1 - y$, $1 - z$

4

V1–V2	3.0453(9)	V3–O6	1.624(3)
V1–O7	1.978(3)	V3–N2	2.060(3)
V1–O8	1.935(3)	V3–N7	2.056(3)
V1–O1	1.639(3)	V2–O7	1.982(3)
V1–O2	1.642(3)	V2–O8	1.942(3)
V1–N1	2.061(3)	V2–O3	1.634(3)
V3–O7	1.971(3)	V2–O4	1.636(3)
V3–O5	1.656(3)	V2–N6	2.056(3)

O7–V1–N1	82.51(2)	O6–V3–N2	97.83(2)
O8–V1–O7	77.84(2)	O6–V3–N7	97.81(2)
O8–V1–N1	157.94(2)	N7–V3–N2	161.54(2)
O1–V1–O7	136.73(2)	O7–V2–N6	81.33(2)
O1–V1–O8	96.47(2)	O8–V2–O7	77.59(2)
O1–V1–O2	108.19(2)	O8–V2–N6	157.70(2)
O1–V1–N1	90.96(2)	O3–V2–O7	117.01(2)
O2–V1–O7	115.04(2)	O3–V2–O8	98.93(2)
O2–V1–O8	100.49(2)	O3–V2–O4	108.49(2)
O2–V1–N1	96.83(2)	O3–V2–N6	97.03(2)
O7–V3–N2	82.83(2)	O4–V2–O7	134.50(2)
O7–V3–N7	82.56(2)	O4–V2–O8	96.80(2)
O5–V3–O7	143.672)	O4–V2–N6	92.77(2)
O5–V3–N2	92.39(2)	V1–O7–V2	100.54(2)
O5–V3–N7	92.71(2)	V3–O7–V1	129.38(2)
O6–V3–O7	110.45(2)	V3–O7–V2	130.01(2)
O6–V3–O5	105.88(2)	V1–O8–V2	103.53(2)

5

V1–O3	2.100(2)	V5–O18	2.096(2)
V1–O4	2.016(2)	V5–O19	2.037(2)
V1–O6	2.023(3)	V5–O21	2.015(2)
V1–O9	1.614(3)	V5–O24	1.617(3)
V1–N2	2.095(3)	V5–N22	2.094(3)
V1–N7	2.081(3)	V5–N27	2.065(3)
V2–O1	2.005(2)	V6–O35	2.006(2)
V2–O3	2.092(2)	V6–O18	2.085(2)
V2–O8	1.613(2)	V6–O23	1.615(2)
V2–N1	2.076(3)	V6–N18	2.103(3)
V2–N6	2.079(3)	V6–N21	2.075(3)
V2–N38	2.101(3)	V6–N26	2.065(3)
V3–O11	2.093(2)	V7–O27	2.088(2)
V3–O12	1.996(3)	V7–O28	2.009(2)
V3–O14	2.001(2)	V7–O30	2.020(2)
V3–O17	1.620(3)	V7–O33	1.615(2)
V3–N11	2.093(3)	V7–N31	2.101(3)
V3–N16	2.071(3)	V7–N37	2.076(3)
V4–O16	1.619(3)	V8–O25	2.021(2)
V4–O11	2.048(2)	V8–O27	2.049(2)
V4–O34	2.024(2)	V8–O32	1.619(2)
V4–N8	2.121(3)	V8–N28	2.113(3)
V4–N12	2.104(3)	V8–N32	2.114(3)
V4–N17	2.081(3)	V8–N36	2.088(3)

O4–V1–O3	78.88(9)	O19–V5–O18	78.02(9)
O4–V1–O6	88.15(1)	O19–V5–N22	86.20(1)
O4–V1–N2	86.76(2)	O19–V5–N27	157.36(2)
O4–V1–N7	157.65(2)	O21–V5–O18	83.60(1)
O6–V1–O3	82.64(1)	O21–V5–O19	86.84(1)
O6–V1–N2	166.45(2)	O21–V5–N22	167.29(2)
O6–V1–N7	92.16(2)	O21–V5–N27	93.60(1)
O9–V1–O3	177.41(2)	O24–V5–O18	176.73(1)
O9–V1–O4	103.43(2)	O24–V5–O19	105.03(1)
O9–V1–O6	98.55(3)	O24–V5–O21	97.67(2)
O9–V1–N2	94.85(3)	O24–V5–N22	94.40(2)
O9–V1–N7	98.62(2)	O24–V5–N27	97.35(2)
N2–V1–O3	84.05(1)	N22–V5–O18	84.56(1)
N7–V1–O3	79.00(1)	N27–V5–O18	79.54(1)
N7–V1–N2	87.82(2)	N27–V5–N22	88.77(2)
O1–V2–O3	85.63(1)	O35–V6–O18	85.92(1)
O1–V2–N1	86.49(2)	O35–V6–N18	90.08(1)
O1–V2–N6	164.91(2)	O35–V6–N21	87.28(1)

O1–V2–N38	90.15(1)	O35–V6–N26	165.59(2)
O3–V2–N38	87.81(1)	O18–V6–N18	86.11(1)
O8–V2–O1	97.59(2)	O23–V6–O35	98.52(1)
O8–V2–O3	175.12(1)	O23–V6–O18	174.95(1)
O8–V2–N1	94.15(2)	O23–V6–N18	96.26(2)
O8–V2–N6	97.07(2)	O23–V6–N21	94.59(2)
O8–V2–N38	95.83(1)	O23–V6–N26	95.79(1)
N1–V2–O3	82.34(1)	N21–V6–O18	83.16(2)
N1–V2–N6	88.91(1)	N21–V6–N18	169.10(2)
N1–V2–N38	169.81(2)	N26–V6–O18	79.71(1)
N6–V2–O3	79.52(1)	N26–V6–N18	90.03(1)
N6–V2–N38	91.89(1)	N26–V6–N21	89.92(1)
O11–V3–N11	82.15(1)	O27–V7–N31	84.63(1)
O12–V3–O11	83.22(1)	O28–V7–O27	83.18(9)
O12–V3–O14	87.95(1)	O28–V7–O30	88.55(1)
O12–V3–N11	165.37(2)	O28–V7–N31	167.81(1)
O12–V3–N16	91.70(2)	O28–V7–N37	93.67(1)
O14–V3–O11	79.56(9)	O30–V7–O27	78.10(9)
O14–V3–N11	88.88(2)	O30–V7–N31	88.74(1)
O14–V3–N16	160.38(2)	O30–V7–N37	158.57(2)
O17–V3–O11	176.92(2)	O33–V7–O27	178.92(2)
O17–V3–O12	99.40(2)	O33–V7–O28	97.70(1)
O17–V3–O14	102.07(2)	O33–V7–O30	102.51(2)
O17–V3–N11	95.23(2)	O33–V7–N31	94.49(2)
O17–V3–N16	97.35(2)	O33–V7–N37	98.31(2)
N16–V3–O11	80.91(1)	N37–V7–O27	81.00(9)
N16–V3–N11	86.54(2)	N37–V7–N31	84.61(2)
O16–V4–O11	175.00(2)	O25–V8–O27	87.07(9)
O16–V4–O34	95.27(2)	O25–V8–N28	91.13(1)
O16–V4–N8	96.10(2)	O25–V8–N32	89.70(1)
O16–V4–N12	93.64(2)	O25–V8–N36	167.48(2)
O16–V4–N17	96.40(2)	O27–V8–N28	88.47(1)
O11–V4–N8	88.51(2)	O27–V8–N32	83.04(1)
O11–V4–N12	81.68(2)	O27–V8–N36	80.83(1)
O11–V4–N17	81.53(2)	O32–V8–O25	96.16(2)
O34–V4–O11	86.40(1)	O32–V8–O27	174.89(1)
O34–V4–N8	92.84(1)	O32–V8–N28	95.40(2)
O34–V4–N12	88.57(2)	O32–V8–N32	93.00(2)
O34–V4–N17	167.14(2)	O32–V8–N36	95.69(2)
N12–V4–N8	169.99(2)	N28–V8–N32	171.42(2)
N17–V4–N8	91.26(1)	N36–V8–N28	91.76(1)
N17–V4–N12	85.33(2)	N36–V8–N32	85.66(1)

Table S3. Hydrogen bonds observed in $[V_2O_2(cit)(Hdatrz)_3]\cdot5H_2O$ (**1**), $[V_2O_2(cit)(Hdatrz)_3][V_2O_2(cit)_2]_{½}\cdot2H_2datrz\cdot9.5H_2O$ (**2**), $V_6O_6(\mu_3\text{-}O)_2(cit)_2(Hdatrz)_4]\cdot4H_2O$ (**3**), $[V_3O_6(\mu_2\text{-}OH)(\mu_3\text{-}O)(Hdatrz)_2]\cdot4.5H_2O$ (**4**) and $K_2\{[V^{IV/V}{}_2O_2(cit)(Hdatrz)(datrz)]_2[V^{IV}{}_2O_2(cit)(Hdatrz)(datrz)]_2\}\cdot27.5H_2O$ (**5**), respectively.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A(°)
1				
N8–H8···O3[a]	0.88(2)	1.99(2)	2.769(4)	146.22(2)
N9–H9A···O7[a]	0.88(2)	2.06(3)	2.821(2)	144.66(2)
N9–H9A···O8[b]	0.88(3)	2.18(1)	2.896(2)	138.47(1)
N10–H10A···O8[c]	0.88(2)	2.25(2)	2.896(2)	129.44(1)
N12–H12···O5[d]	0.88(1)	2.01(2)	2.750(2)	140.38(2)

Symmetric codes: (a) -1 + *x*, *y*, *z*; (b) 1 – *x*, ½ + *y*, ½ – *z*; (c) 1 – *x*, -½ + *y*, ½ – *z*; (d) 1 – *x*, 1 – *y*, – *z*

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A(°)
2				
N3–H3···O15[a]	0.87(1)	1.95(2)	2.811(2)	170.20(3)
N4–H4B···O17[b]	0.87(2)	2.09(3)	2.944(2)	169.00(3)
N5–H5B···O16[a]	0.87(3)	2.11(3)	2.897(2)	149.20(2)
N8–H8···O2[c]	0.87(2)	1.93(2)	2.658(2)	141.20(2)
N9–H9A···O16	0.87(2)	2.23(2)	2.900(2)	134.20(2)
N10–H10B···O5[c]	0.87(1)	2.09(2)	2.960(2)	175.21(2)
N12–H12···O7[d]	0.87(3)	1.99(2)	2.728(2)	141.50(1)
N15–H15A···O6[d]	0.87(2)	2.17(2)	2.991(2)	158.22(3)
N18–H18B···O10[b]	0.87(2)	2.10(2)	2.921(2)	158.12(2)
N19–H19B···O11[b]	0.87(2)	2.14(3)	2.927(6)	149.50(4)
N9–H9B···O11[b]	0.87(2)	2.14(2)	2.923(2)	149.50(4)

Symmetric codes: (a) *x*, -1 + *y*, *z*; (b) 2 – *x*, 2 – *y*, -*z*; (c) 1 + *x*, *y*, *z*; (d) 2 – *x*, 2 – *y*, 1 – *z*

3

N5–H5A···O1	0.88(2)	2.15(2)	2.858(3)	137.24(2)
N9–H9A···O4	0.88(3)	2.16(3)	2.872(3)	137.24(2)
N4–H4A···O7[a]	0.88(2)	2.47(2)	3.081(3)	117.16(2)
N10–H10A···O7[a]	0.88(3)	2.35(2)	3.002(3)	130.65(2)
N3–H3···O2[b]	0.88(2)	2.13(2)	2.808(3)	132.56(2)
N4–H4B···O2[b]	0.88(2)	2.06(1)	2.816(3)	143.21(2)
N8–H8···O5[c]	0.88(3)	2.58(3)	3.174(3)	125.32(2)
N4–H4A···O11[d]	0.88(2)	2.13(3)	2.873(3)	142.22(2)
N8–H8···O8[e]	0.88(2)	2.24(2)	2.929(3)	135.35(1)
N10–H10B···O5[e]	0.88(3)	1.93(2)	2.758(3)	155.64(2)
N5–H5B···O9[f]	0.88(2)	2.27(3)	3.027(3)	143.69(2)

Symmetric codes: (a) $1 - x$, $1 - y$, $1 - z$; (b) $½ + x$, $3/2 - y$, $-½ + z$; (c) $½ + x$,$1/2 - y$, $-½ + z$; (d) $1 - x$, $1 - y$, $2 - z$; (e) $3/2 - x$, $½ + y$, $3/2 - z$; (f) $3/2 - x$, $-½ + y$, $3/2 - z$

4

N8–H8···O8[a]	0.88(2)	1.79(2)	2.605(4)	153.70(2)

Symmetric codes: (a) $½ + x$, $½ - y$, $-½ + z$

5

N20–H20A···O16	0.88(2)	2.34(2)	2.971(7)	128.30(8)
N39–H39A···O32	0.88(3)	2.36(1)	2.954(1)	125.20(7)
N3–H3···O20[a]	0.88(1)	1.93(2)	2.750(1)	155.10(2)
N13–H13···O30[b]	0.88(2)	1.97(3)	2.776(1)	151.01(8)
N23–H23···O5[c]	0.88(3)	1.87(2)	2.741(1)	169.50(8)
N25–H25B···O2[c]	0.88(2)	2.09(2)	2.972(1)	177.40(9)
N33–H33···O15[d]	0.88(2)	1.93(3)	2.786(1)	164.01(7)

(c) $\frac{1}{2} + x$, $3/2 - y$, $-\frac{1}{2} + z$; (d) $\frac{1}{2} + x$, $3/2 - y$, $\frac{1}{2} + z$

Table S4. Bond valence sum calculations for **1–5**, respectively.

Complexes	Atoms	n	s	|d|	Assignment
1	V1	4	4.226	0.226	
	V2	4	4.206	0.206	
	average	**4**	**4.216**	**0.216**	
2a	V1	4	4.247	0.247	
	V2	4	4.280	0.280	
	average	**4**	**4.264**	**0.264**	
2b	V3	4	4.025	0.025	
3	V1	4	4.089	0.089	
	V2	4	4.099	0.099	
	V3	4	4.218	0.218	
	average	**4**	**4.135**	**0.135**	
	O10	2	2.172		μ_3-O^{2-}
4	V1	5	5.207	0.207	
	V2	5	5.143	0.143	
	V3	5	5.187	0.187	
	average	**5**	**5.179**	**0.179**	
	O7	1	1.394		μ_2-OH^-
	O8	2	1.876		μ_3-O^{2-}
5	V1	4	4.192	0.192	
	V2	5	4.733	0.267	
	V3	4	4.182	0.182	
	V4	4	4.201	0.201	
	V5	4	4.193	0.193	
	V6	5	4.758	0.242	
	V7	4	4.215	0.215	
	V8	4	4.188	0.188	