Supporting materials

Protonated and deprotonated vanadyl imidazole tartrates for the mimics of the vanadium coordination in FeV-cofactor of V-nitrogenase

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Figure and Table Options

Figure S1. 2D layered structure of $(H_2im)_2[\Delta,\Lambda\text{-}V^{IV}{}_2O_2(R,R\text{-}H_2tart)(R,R\text{-}tart)(Him)_2]\cdot Him$ (**1**).

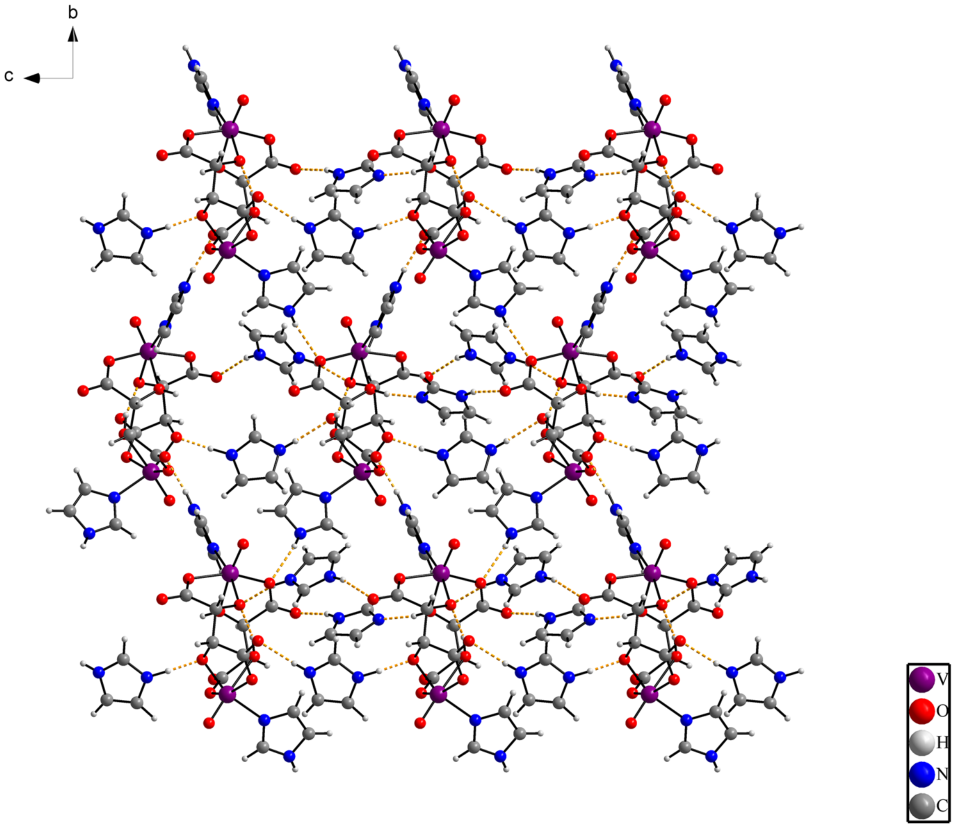


Figure S2. 2D layered structure of [Λ,Λ-$V^{IV}_2O_2$(*R*,*R*-tart)$(Him)_6$]·$4H_2O$ (**2**).

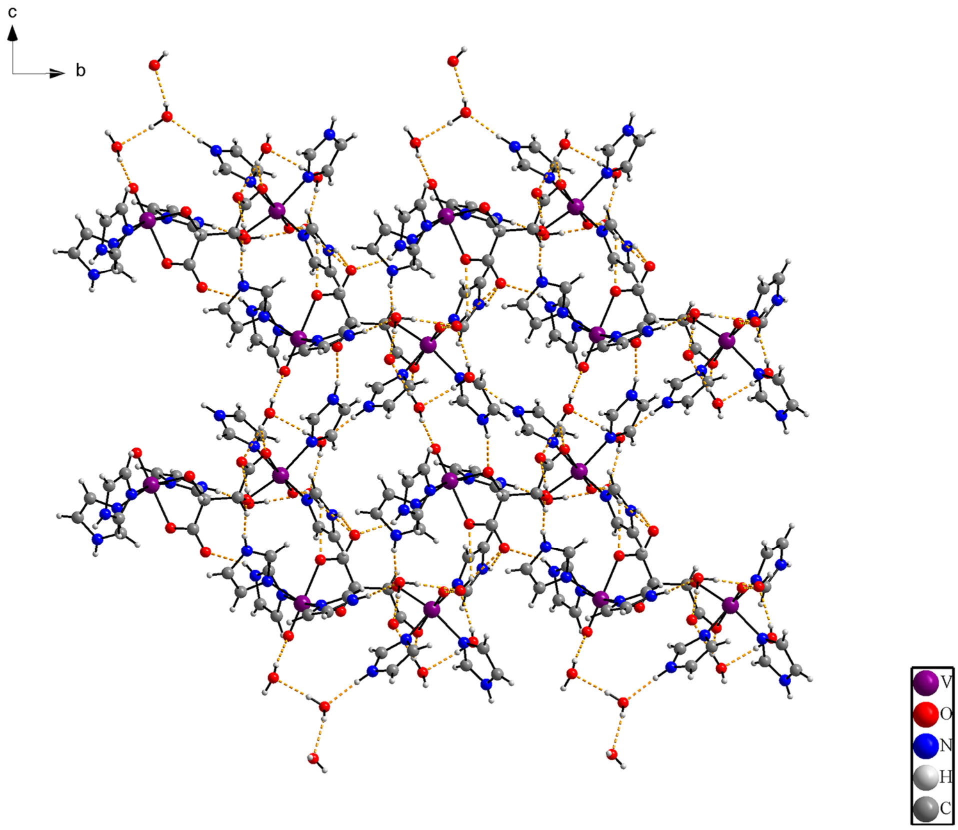


Figure S3. ORTEP plot of the anion structure $(H_2im)_2[\Lambda,\Delta\text{-}V^{IV}{}_2O_2(S,S\text{-}H_2tart)(S,S\text{-}tart)(Him)_2]\cdot Him$ (**3**) at the 30% probability levels.

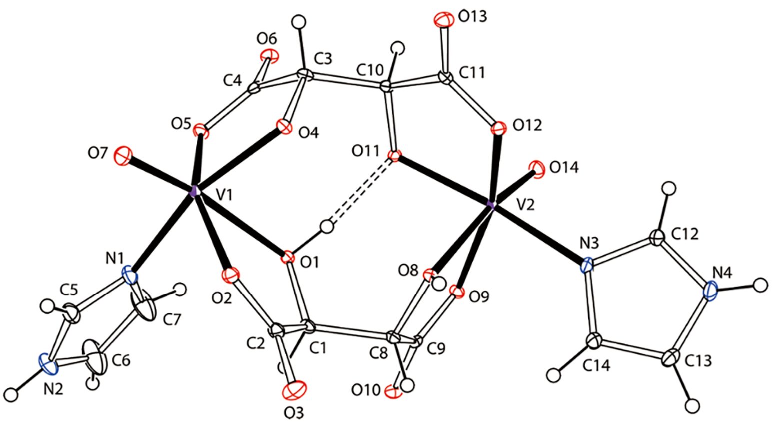


Figure S4. ORTEP plot of the molecular structure [Δ,Δ-$V^{IV}_2O_2$(S,S-tart)(Him)$_6$]·4H_2O (**4**) at the 30% probability levels.

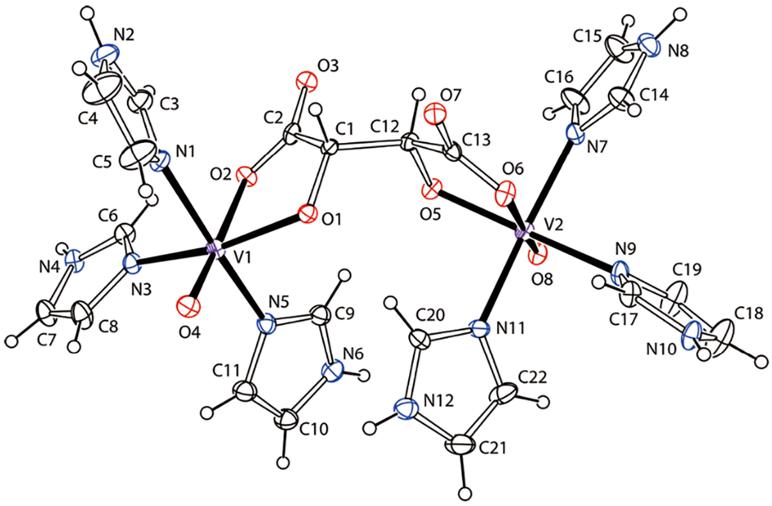
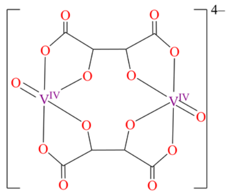


Figure S5. Chemdraw structures for oxidovanadium tartrates **5** – **8**, other oxidovanadium hydroxycarboxylates **9** – **16** and reported FeV-cos **17** – **21**.



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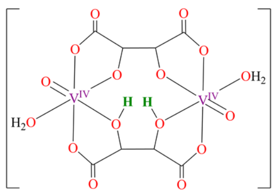

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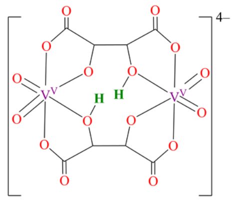

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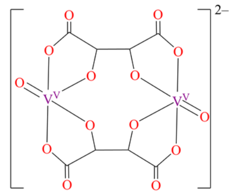

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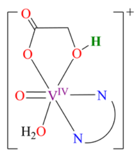

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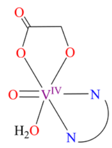

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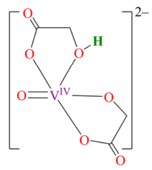

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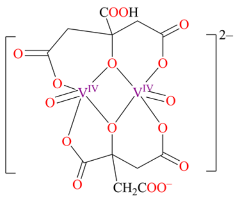

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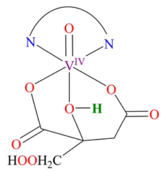

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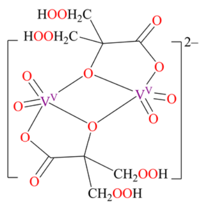

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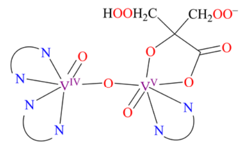

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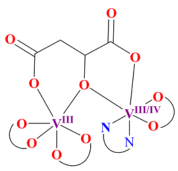

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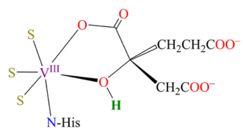
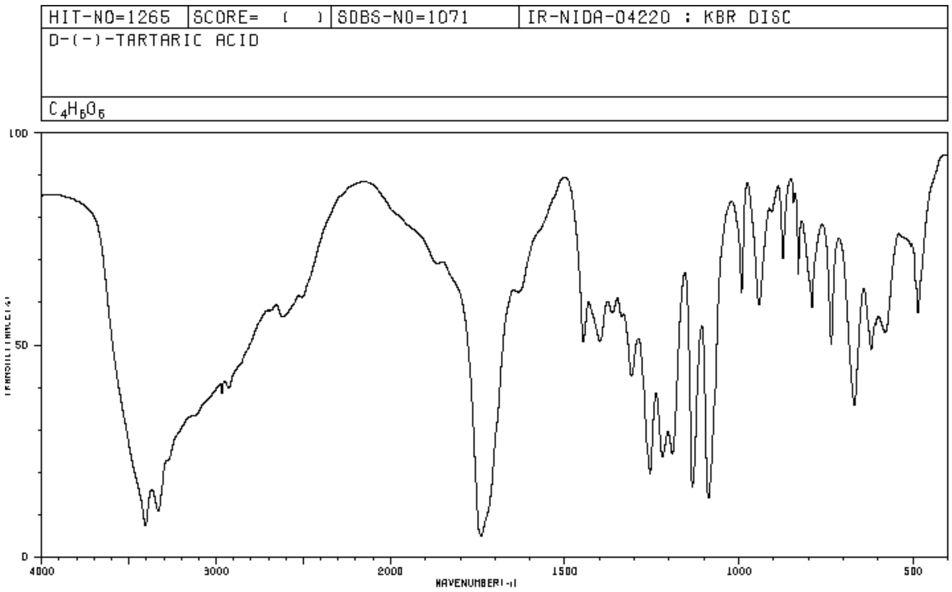


17 – **21**

Figure S6. FT-IR spectrum of *R*,*R*-tartaric acid originated from Spectral Database for Organic Compounds SDBS. URL for this compound: https://sdbs.db.aist.go.jp/sdbs/cgi-bin/landingpage?sdbsno=1071.



3406	7	1400	49	1087	13	736	47
3332	10	1364	55	992	60	669	34
2967	37	1308	41	942	57	620	47
2928	38	1266	18	873	68	580	60
2613	55	1219	22	843	81	486	55
1740	4	1191	29	830	84		
1446	49	1134	16	790	67		

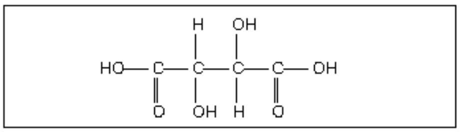
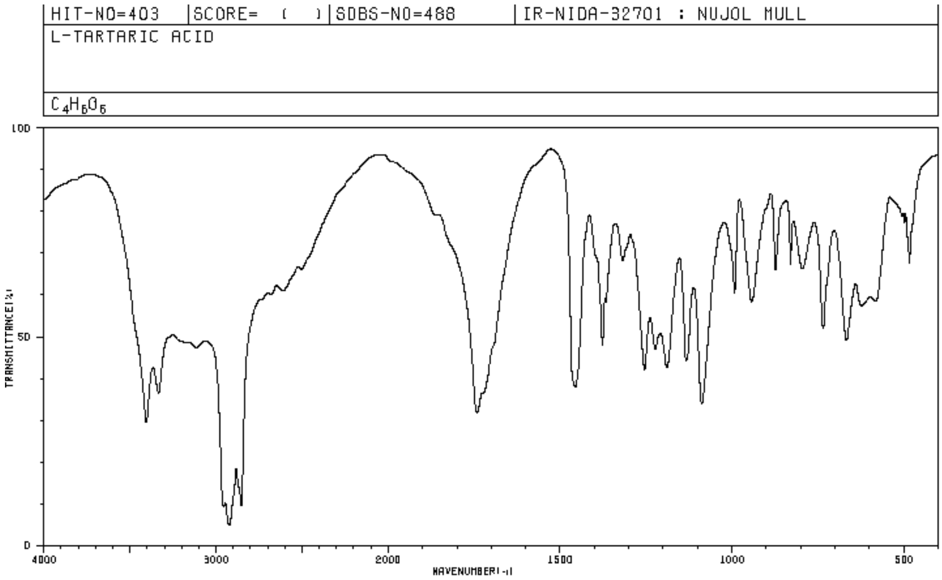


Figure S7. FT-IR spectrum of *S*, *S*-tartaric acid originated from Spectral Database for Organic Compounds SDBS. URL for this compound: https://sdbs.db.aist.go.jp/sdbs/cgi-bin/landingpage?sdbsno=488.



3406	26	1741	31	1189	41	796	64	486	66
3334	35	1456	36	1133	42	735	50		
3114	46	1378	46	1087	33	667	47		
2924	4	1366	67	992	68	624	66		
2868	13	1318	66	943	57	617	55		
2854	9	1255	41	874	84	500	74		
2609	68	1224	44	830	64	491	70		

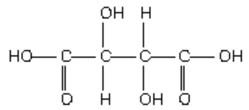


Figure S8a. VCD and IR spectra of $(H_2im)_2[\Delta,\Lambda\text{-}V^{IV}{}_2O_2(R,R\text{-}H_2tart)(R,R\text{-}tart)(Him)_2]\cdot Him$ (**1**) with KBr pellet.

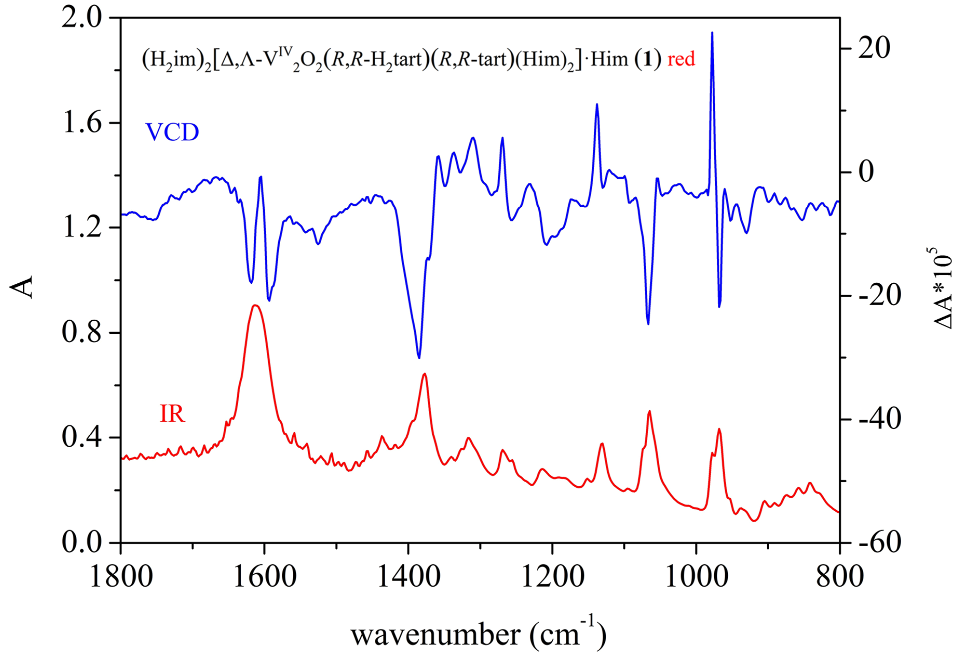


Figure S8b. VCD and IR spectra of [Λ,Λ-$V^{IV}_2O_2$(*R*,*R*-tart)$(Him)_6$]·$4H_2O$ (**2**) with KBr pellet.

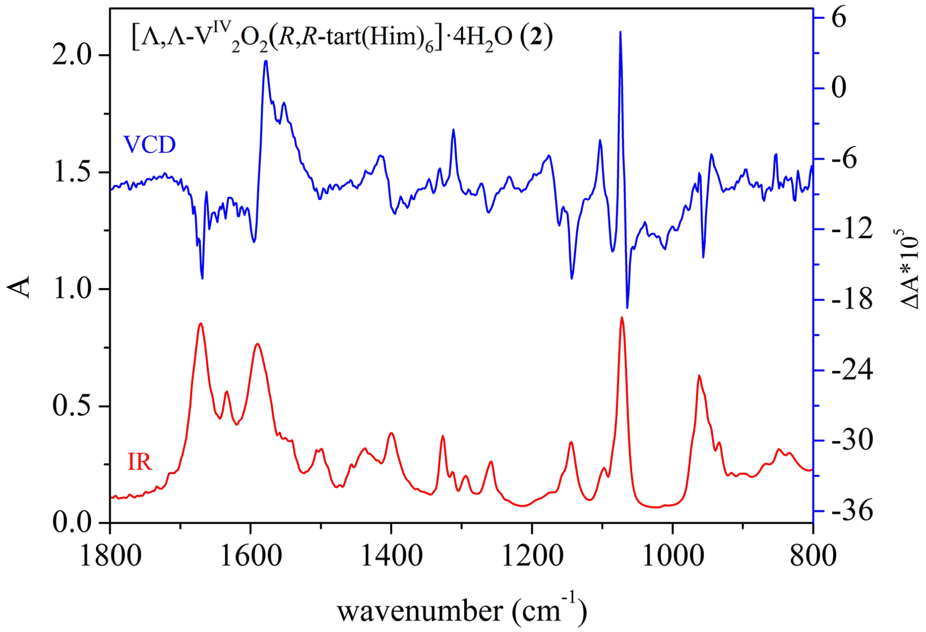


Figure S8c. VCD and IR spectra of $(H_2im)_2[\Lambda,\Delta\text{-}V^{IV}{}_2O_2(S,S\text{-}H_2tart)(S,S\text{-}tart)(Him)_2]\cdot Him$ (**3**) with KBr pellet.

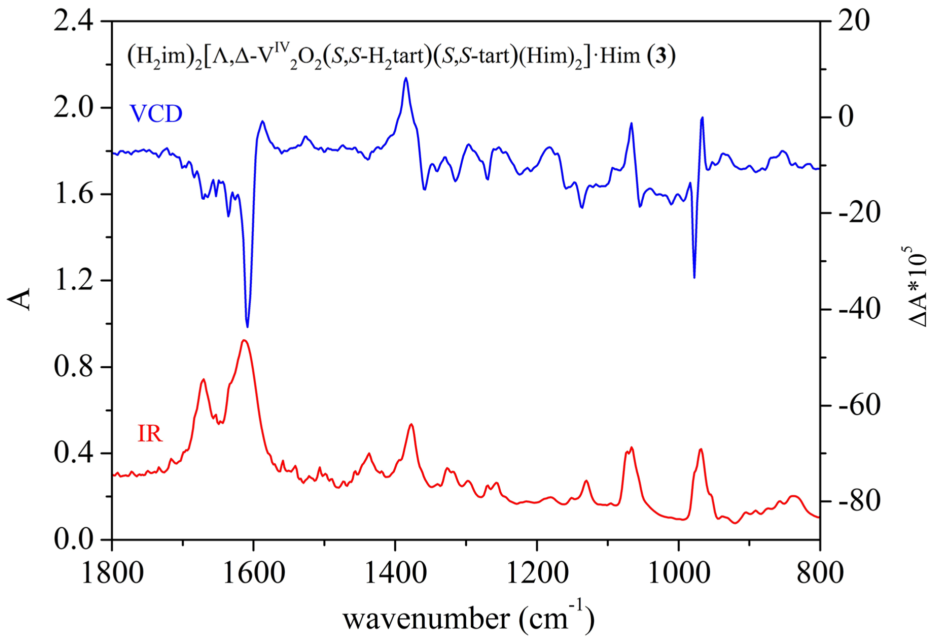


Figure S8d. VCD and IR spectra of [Δ,Δ-$V^{IV}_2O_2$(*S*,*S*-tart)$(Him)_6$]·$4H_2O$ (**4**) with KBr pellet.

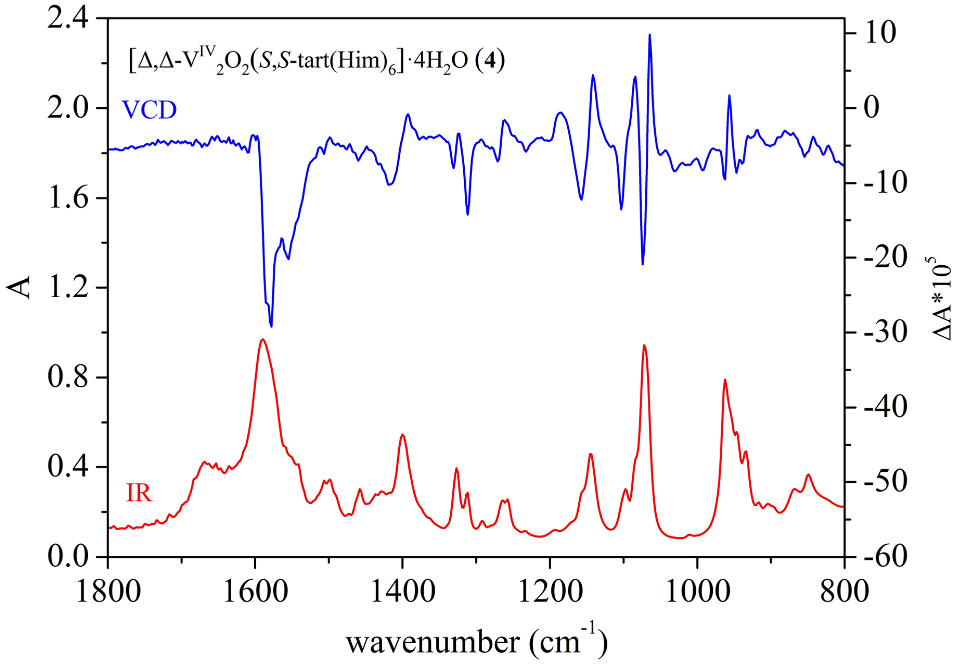


Figure S9. X-band EPR spectra of **1** and **3** in solid-states (a) and **1** in H_2O (b) at 298 K, respectively.

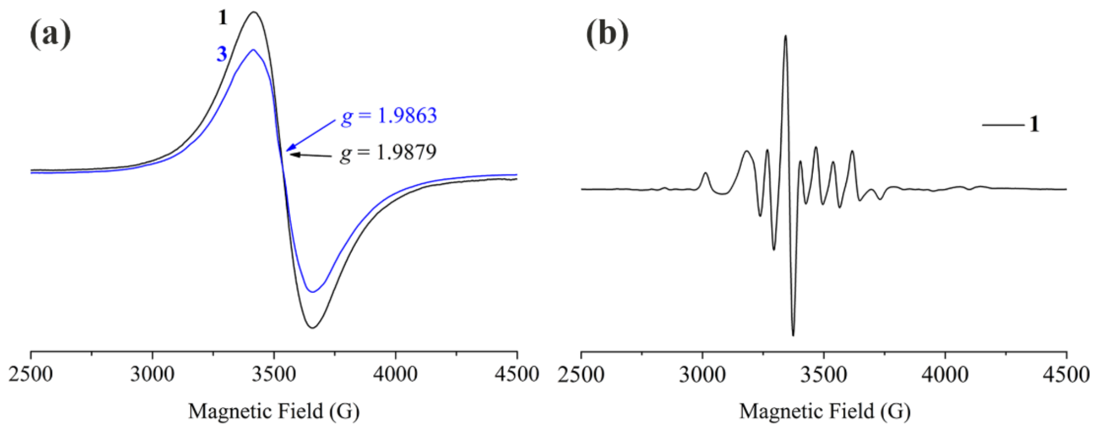


Figure S10. X-band EPR spectra with *g*-axis in solid state of **1** – **4** at 298 K, respectively.

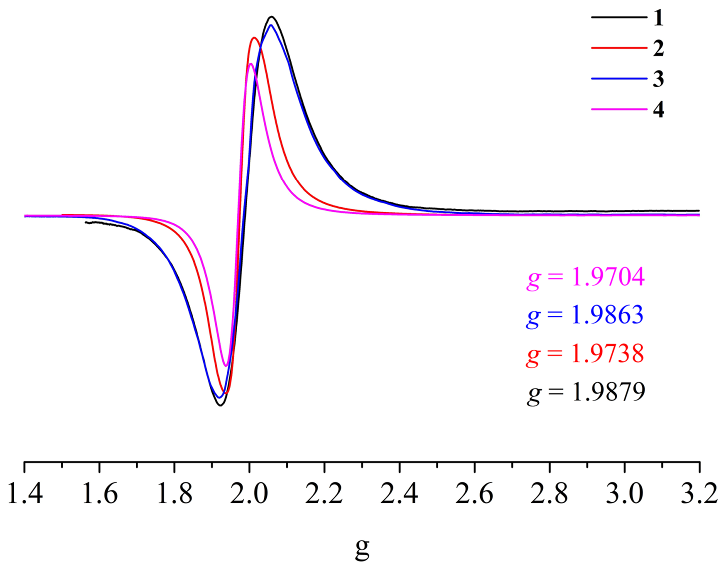


Figure S11. Temperature-dependence magnetic susceptibility of **2** in an applied field of B = 0.1 T over the range of 2 – 300 K. Red line correspond to the best fitting result.

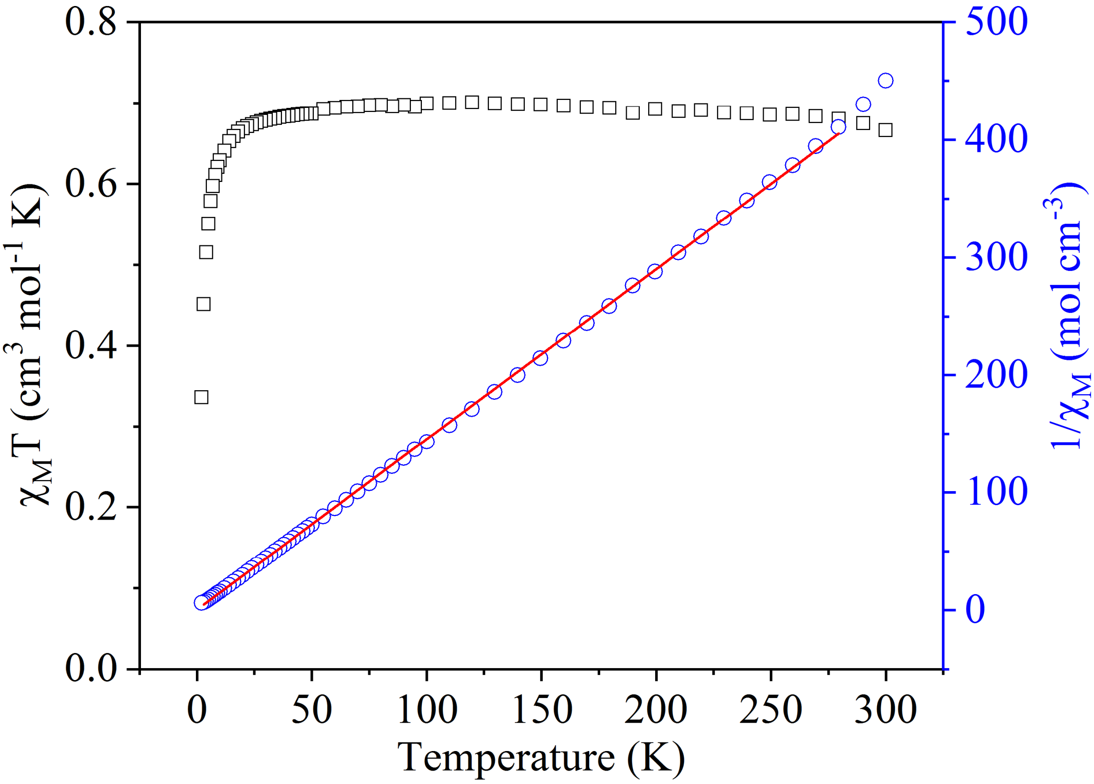


Figure S12. IR spectra of $(H_2im)_2[\Delta,\Lambda\text{-}V^{IV}{}_2O_2(R,R\text{-}H_2tart)(R,R\text{-}tart)(Him)_2]\cdot Him$ (**1**), $[\Lambda,\Lambda\text{-}V^{IV}{}_2O_2(R,R\text{-}tart)(Him)_6]\cdot 4H_2O$ (**2**), $(H_2im)_2[\Lambda,\Delta\text{-}V^{IV}{}_2O_2(S,S\text{-}H_2tart)(S,S\text{-}tart)(Him)_2]\cdot Him$ (**3**) and $[\Delta,\Delta\text{-}V^{IV}{}_2O_2(S,S\text{-}tart)(Him)_6]\cdot 4H_2O$ (**4**), respectively.

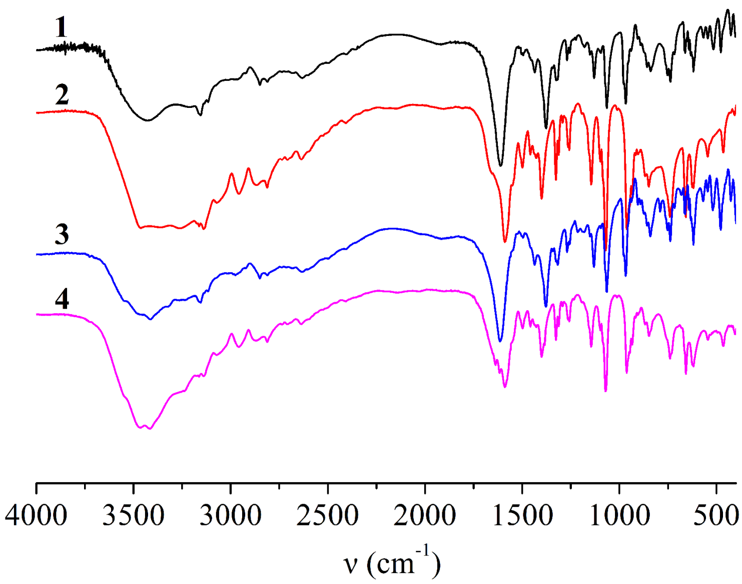


Figure S13. (a) Diffused reflectance UV-Vis spectra of solids $(H_2im)_2$[Δ,Λ-$V^{IV}_2O_2$(*R*,*R*-H_2tart)(*R*,*R*-tart)$(Him)_2$]·Him (**1**), [Λ,Λ-$V^{IV}_2O_2$(*R*,*R*-tart)$(Him)_6$]·4H_2O (**2**), $(H_2im)_2$[Λ,Δ-$V^{IV}_2O_2$(*S*,*S*-H_2tart)(*S*,*S*-tart)$(Him)_2$]·Him (**3**) and [Δ,Δ-$V^{IV}_2O_2$(*S*,*S*-tart)$(Him)_6$]·4H_2O (**4**), respectively. (b) Comparisons for solid and solution UV-Vis spectum of [Λ,Λ-$V^{IV}_2O_2$(*R*,*R*-tart)$(Him)_6$]·4H_2O (**2**) in water (inset: UV-Vis spectra with local amplification regions).

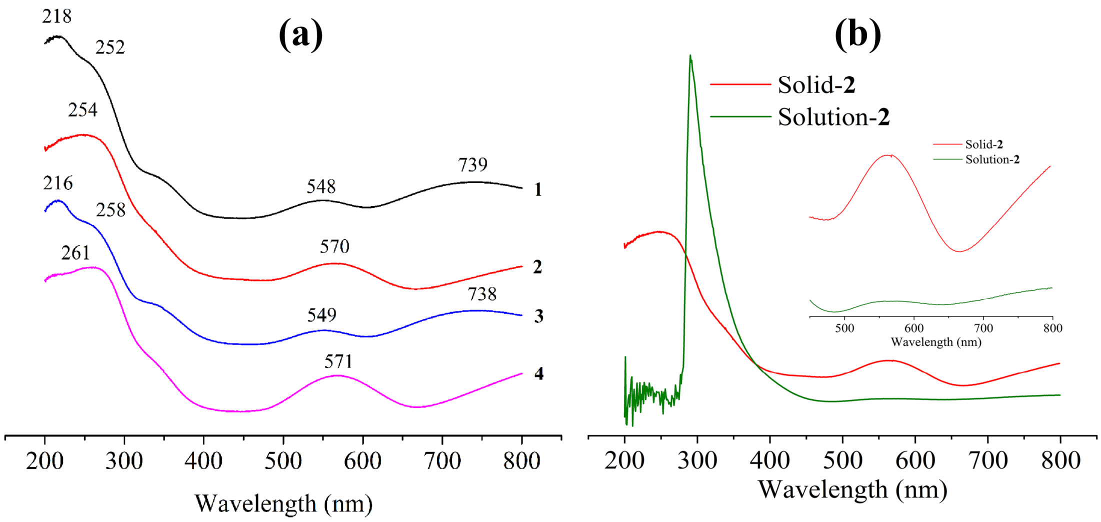


Figure S14. TG–DTG curves of $(H_2im)_2[\Delta,\Lambda\text{-}V^{IV}{}_2O_2(R,R\text{-}H_2tart)(R,R\text{-}tart)(Him)_2]\cdot Him$ (**1**, a); TG–DTG curves of $[\Lambda,\Lambda\text{-}V^{IV}{}_2O_2(R,R\text{-}tart)(Him)_6]\cdot 4H_2O$ (**2**, b); TG–DTG curves of $(H_2im)_2[\Lambda,\Delta\text{-}V^{IV}{}_2O_2(S,S\text{-}H_2tart)(S,S\text{-}tart)(Him)_2]\cdot Him$ (**3**, c); TG–DTG curves of $[\Delta,\Delta\text{-}V^{IV}{}_2O_2(S,S\text{-}tart)(Him)_6]\cdot 4H_2O$ (**4**, d).

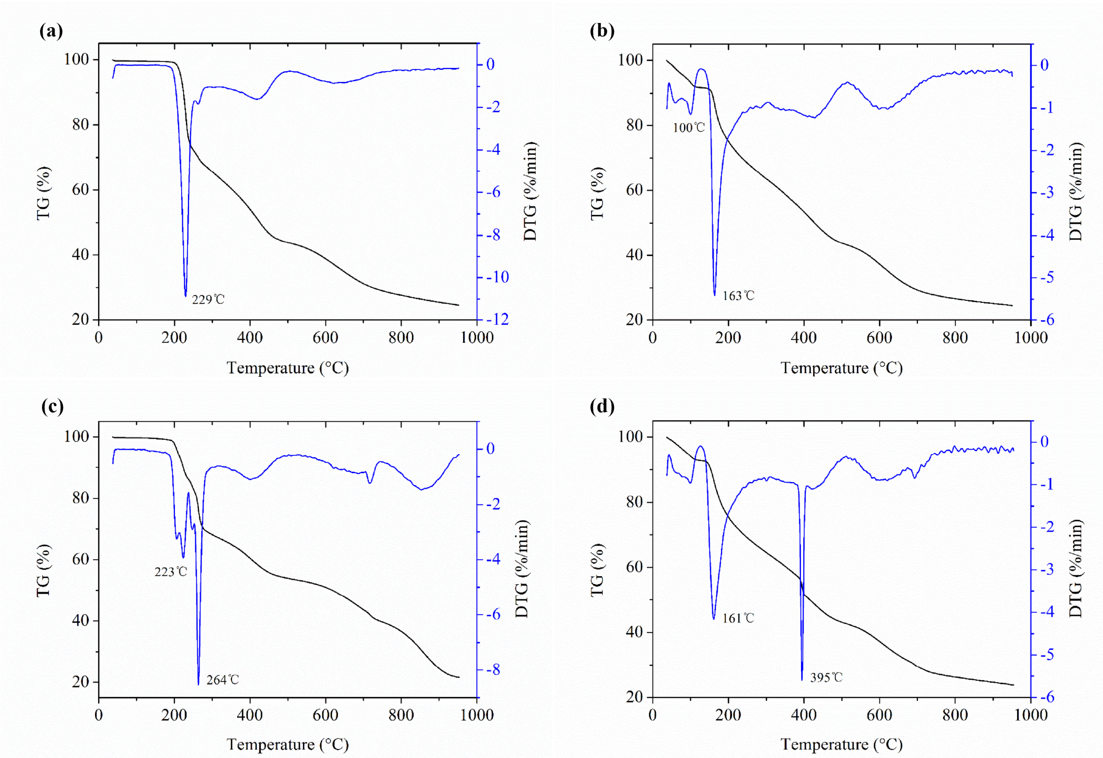


Figure S15. Cyclic voltammogram of [Λ,Λ-V_2O_2(*R*,*R*-tart)(Him)$_6$]·$4H_2O$ (**2**) in anhydrous DMF with 0.10 M [n-Bu_4N]ClO_4 at a glassy carbon electrode with scan rate of 50 mV·s^{-1} (a) and various scan rates (b), respectively. (c) Plots of redox peak currents against $\nu^{1/2}$. (d) Differential pulse voltammogram of **2**.

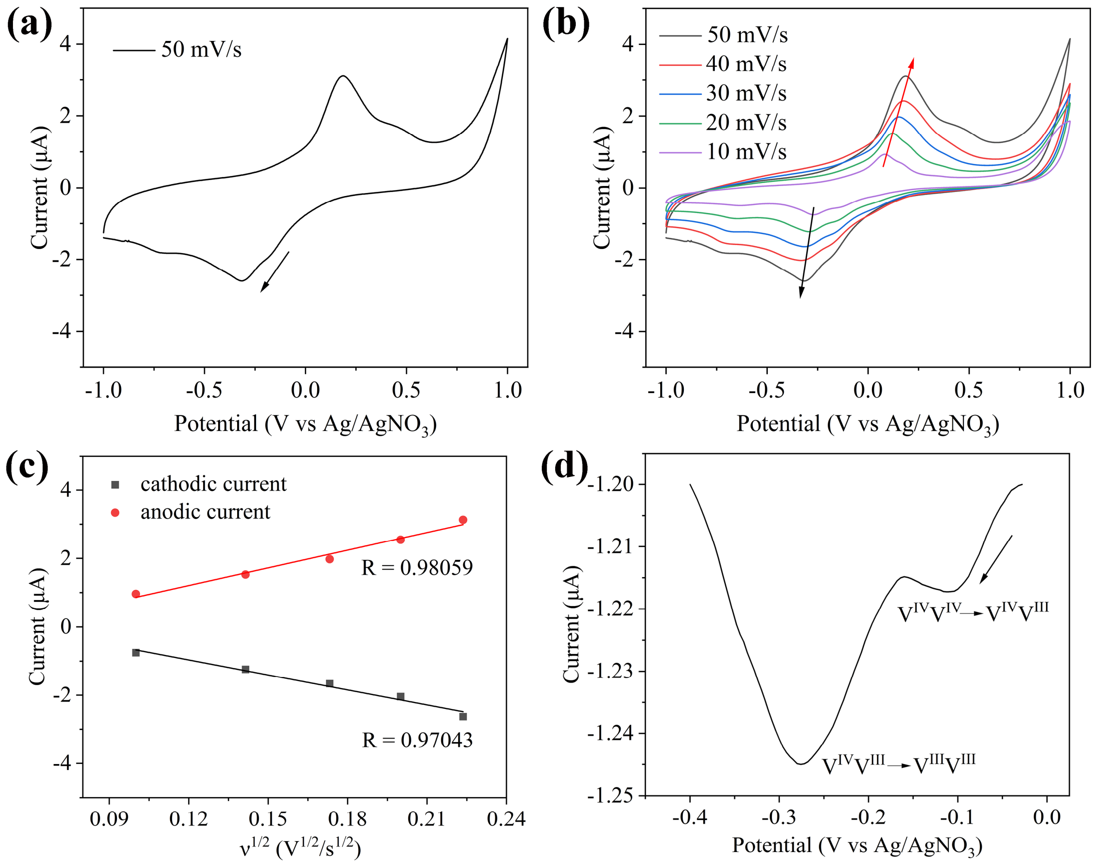


Figure S16. Comparison of the observed PXRD (red) with the simulated patterns (black) calculated from the crystal data for [Λ,Λ-$V^{IV}_2O_2$(*R*,*R*-tart)(Him)$_6$]·4H_2O (**2**).

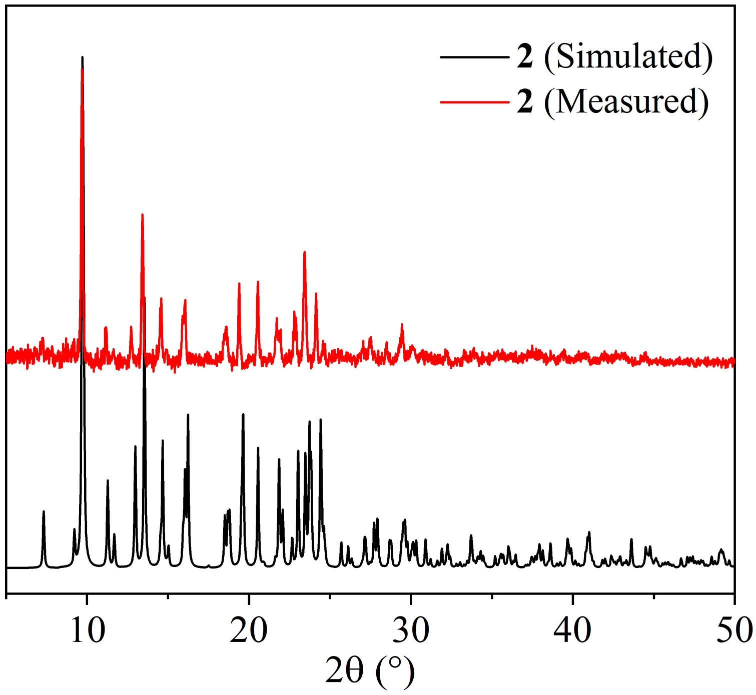


Table S1. Crystallographic data and structural refinements for complexes $(H_2im)_2[\Delta,\Lambda\text{-}V^{IV}{}_2O_2(R,R\text{-}H_2tart)(R,R\text{-}tart)(Him)_2]\cdot Him$ (**1**), $[\Lambda,\Lambda\text{-}V^{IV}{}_2O_2(R,R\text{-}tart)(Him)_6]\cdot 4H_2O$ (**2**), $(H_2im)_2[\Lambda,\Delta\text{-}V^{IV}{}_2O_2(S,S\text{-}H_2tart)(S,S\text{-}tart)(Him)_2]\cdot Him$ (**3**) and $[\Delta,\Delta\text{-}V^{IV}{}_2O_2(S,S\text{-}tart)(Him)_6]\cdot 4H_2O$ (**4**), respectively.

	1	**2**	**3**	**4**
Empirical formula	$C_{23}H_{28}N_{10}O_{14}V_2$	$C_{22}H_{34}N_{12}O_{12}V_2$	$C_{23}H_{28}N_{10}O_{14}V_2$	$C_{22}H_{34}N_{12}O_{12}V_2$
Formula weight	770.43	760.49	770.43	760.49
Temperature/K	173(1)	100(1)	100(1)	100(1)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P\,2_1$	$P\,2_1$	$P\,2_1$	$P\,2_1$
a/Å	8.9068(3)	10.1662(1)	8.8863(1)	10.1454(2)
b/Å	19.6606(6)	13.6125(1)	19.5997(1)	13.6326(2)
c/Å	9.8849(4)	12.8047(1)	9.8686(1)	12.7784(2)
α/°	90	90	90	90
β/°	109.160(4)	109.405(1)	108.907(1)	109.196(2)
γ/°	90	90	90	90
Volume/Å^3	1635.1(1)	1671.35(3)	1626.07(3)	1669.09(5)
Z	2	2	2	2
ρ_{calc}g/cm^3	1.565	1.511	1.574	1.513
μ/mm^{-1}	0.652	5.352	5.544	5.359
F(000)	788	784	788	784
Crystal size/mm^3	0.4 × 0.3 × 0.2	0.1 × 0.1 × 0.1	0.2 × 0.2 × 0.2	0.2 × 0.15 × 0.15
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)

2θ range for data collection/°	4.362 to 49.98	7.32 to 155.708	9.474 to 155.064	7.326 to 156.334
Reflections collected	5991	22233	16285	11514
Independent reflections	4595	6846	4870	5339
R_{int}	0.0298	0.0301	0.0249	0.0318
Data/restraints/parameters	4595/188/472	6846/2/469	4870/16/449	5339/26/469
Goodness of fit on F^2	1.043	1.036	1.083	1.161
Final R indexes [$I>=2\sigma (I)$]	R_1 = 0.0377, wR_2 = 0.0904	R_1 = 0.0257, wR_2 = 0.0662	R_1 = 0.0266, wR_2 = 0.0698	R_1 = 0.0384, wR_2 = 0.1091
Final R indexes [all data]	R_1 = 0.0405, wR_2 = 0.0932	R_1 = 0.0300, wR_2 = 0.0695	R_1 = 0.0289, wR_2 = 0.0713	R_1 = 0.0481, wR_2 = 0.1233
Largest diff. peak/hole / e Å^{-3}	0.40/-0.36	0.23/-0.39	0.24/-0.53	0.74/-0.74
Flack parameter	0.02(2)	-0.002(2)	0.009(3)	0.005(5)

Table S2. Selected hydrogen bonds (Å) in $(H_2im)_2[\Delta,\Lambda\text{-}V^{IV}{}_2O_2(R,R\text{-}H_2tart)(R,R\text{-}tart)(Him)_2]\cdot Him$ (**1**).

Donor–H···Acceptor	D–H(Å)	H···A(Å)	D···A(Å)	D–H···A(°)
O(4)–H(4)···N(9)	0.86(3)	1.69(2)	2.530(6)	169(4)
O(11)–H(11)···O(1)	0.88(2)	1.92(2)	2.731(5)	153(3)
N(2)–H(2)···O(13)[a]	0.88	1.82	2.695(7)	175
N(4)–H(4A)···O(5)[b]	0.79(9)	2.08(8)	2.836(7)	160(8)
N(5)–H(5A)···O(1)	0.88	1.89	2.755(5)	167
N(6)–H(6A)···O(2)[c]	0.88	2.54	3.093(5)	121
N(6)–H(6A)…O(3)[c]	0.88	2.02	2.876(6)	163
N(7)–H(7A)···O(8)	0.98(8)	1.60(7)	2.573(6)	175(9)
N(8)–H(8A)···O(10)[d]	0.80(6)	1.94(6)	2.723(6)	167(6)
N(10)–H(10A)···O(6)[d]	0.88	1.95	2.811(6)	166

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

Table S3. Selected hydrogen bonds (Å) in [Λ,Λ-$V^{IV}_2O_2$(*R*,*R*-tart)$(Him)_6$]·$4H_2O$ (**2**).

Donor–H···Acceptor	D–H(Å)	H···A(Å)	D···A(Å)	D–H···A(°)
O(1w)–H(1wA)···O(7)	0.84(5)	1.88(5)	2.719(3)	176(6)
O(1w)–H(1wB)···O(2w)[a]	0.84(7)	2.05(7)	2.886(4)	174(5)
O(2w)–H(2wA)···O(2)[b]	0.76(5)	2.56(5)	3.104(3)	131(5)
O(2w–H(2wA)···O(3)[b]	0.76(5)	2.14(5)	2.889(3)	172(5)
O(2w)–H(2wB)···O(8)[c]	0.75(5)	1.96(5)	2.697(4)	171(5)
O(3w)–H(3wA)···O(2w)	0.82(6)	2.01(6)	2.767(4)	153(6)
O(3w)–H(3wB)···O(4w)	0.85(3)	1.88(4)	2.703(4)	162(6)
O(4w)–H(4wB)···O(4)	0.83(5)	1.98(5)	2.803(3)	172(5)
O(4w)–H(4wA)···O(7)[d]	0.87(5)	1.88(5)	2.741(3)	170(5)
N(2)–H(2)···O(3)[e]	0.86(5)	2.10(4)	2.885(4)	151(4)
N(4)–H(4)···O(5)[f]	0.86	1.93	2.778(3)	168
N(6)–H(6)···O(1w)[g]	0.86	1.97	2.816(4)	169
N(8)–H(8)···O(3)[h]	0.86	2.03	2.822(4)	153
N(10)–H(10)···O(1)	0.86	1.92	2.756(3)	165
N(12)–H(12)···O(3w)	0.86	1.86	2.722(4)	176

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

Table S4. Selected hydrogen bonds (Å) in $(H_2im)_2[\Lambda,\Delta\text{-}V^{IV}{}_2O_2(S,S\text{-}H_2tart)(S,S\text{-}tart)(Him)_2]\cdot Him$ (**3**).

Donor–H···Acceptor	D–H(Å)	H···A(Å)	D···A(Å)	D–H···A(°)
O(1)–H(1)···O(4)	0.90(5)	2.49(5)	2.802(2)	101(4)
O(1)–H(1)···O(8)	0.90(5)	2.34(5)	2.812(3)	112(4)
O(1)–H(1)···O(11)	0.90(5)	1.85(6)	2.724(3)	163(4)
N(2)–H(2)···O(9)^{a}	0.86	2.01	2.819(4)	157
N(4)–H(4)···O(3)^{b}	0.86	1.83	2.686(4)	174
N(5)–H(5A)···O(4)	0.86	1.75	2.565(3)	158
N(6)–H(6A)···O(6)^{c}	0.86	1.9	2.720(3)	158
N(7)–H(7A)···O(11)	0.86	1.9	2.742(3)	166
O(8)–H(8)···N(9)	0.87(2)	1.65(2)	2.509(3)	171(3)
N(8)–H(8B)···O(12)^{d}	0.86	2.55	3.085(3)	121
N(8)–H(8B)···O(13)^{d}	0.86	2.01	2.837(3)	163
N(10)–H(10A)···O(10)^{c}	0.86	1.96	2.796(3)	166

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

Table S5. Selected hydrogen bonds (Å) in [Δ,Δ-$V^{IV}_2O_2$(*S*,*S*-tart)$(Him)_6$]·$4H_2O$ (**4**).

Donor–H···Acceptor	D–H(Å)	H···A(Å)	D···A(Å)	D–H···A(°)
O(2w)–H(2wA)···O(3)[a]	0.81(7)	1.91(7)	2.723(6)	175(7)
N(2)–H(2)···O(3)[b]	0.86	2.02	2.817(8)	153
O(1w)–H(1wA)···O(4)	0.85(1)	1.85(1)	2.687(8)	172(9)
O(2w)–H(2wB)···O(1w)	0.85(1)	2.04(1)	2.877(10)	172(1)
N(4)–H(4)···O(5)[c]	0.86	1.92	2.759(6)	163
O(1w)–H(1wB)···O(7)[d]	0.68(1)	2.22(1)	2.895(8)	170(1)
O(4w)–H(4wA)···O(1w)[e]	0.87(7)	1.95(7)	2.759(9)	154(7)
N(6)–H(6)···O(4w)	0.86	1.85	2.709(9)	175
O(4w)–H(4wB)···O(3w)	0.85(7)	1.86(7)	2.694(9)	168(1)
O(3w)–H(3wA)···O(3)[f]	0.80(1)	1.95(1)	2.739(7)	168(7)
N(8)–H(8)···O(7)[g]	0.86	2.12	2.878(8)	148
O(3w)–H(3wB)···O(8)	0.86(7)	1.95(7)	2.795(7)	171(7)
N(10)–H(10)···O(1)[h]	0.76(1)	2.03(1)	2.780(7)	172(1)
N(12)–H(12)···O(2w)	0.86	1.96	2.809(9)	169

Symmetric codes: (a) 1 + *x*, *y*, *z*; (b) -*x*, -½ + *y*, 2 – *z*; (c) -*x*, -½ + *y*, 1 – *z*; (d) 1 – *x*, -½ + *y*, 2 – *z*; (e) 1 – *x*, 1/2 + *y*, 1 – *z*; (f) -*x*, ½ + *y*, 1 – *z*; (g) -*x*, ½ + *y*, 2 – *z*; (h) 1 – *x*, ½ + *y*, 2 – *z*.

Table S6. Selected bond distances (Å) and angles (°) for $(H_2im)_2[\Delta,\Lambda\text{-}V^{IV}{}_2O_2(R,R\text{-}H_2tart)(R,R\text{-}tart)(Him)_2]\cdot Him$ (**1**).

1			
V(1)–O(1)	1.989(3)	V(2)–O(8)	1.961(3)
V(1)–O(2)	1.987(3)	V(2)–O(9)	1.990(4)
V(1)–O(4)	2.155(3)	V(2)–O(11)	2.318(3)
V(1)–O(5)	2.051(3)	V(2)–O(12)	2.007(3)
V(1)–O(7)	1.603(4)	V(2)–O(14)	1.595(4)
V(1)–N(1)	2.130(4)	V(2)–N(3)	2.126(4)
O(1)–V(1)–O(5)	90.1(1)	O(8)–V(2)–O(11)	81.5(1)
O(1)–V(1)–O(4)	84.9(1)	O(8)–V(2)–O(9)	81.4(1)
O(1)–V(1)–N(1)	166.2(2)	O(8)–V(2)–O(12)	90.4(2)
O(2)–V(1)–O(5)	159.3(1)	O(8)–V(2)–N(3)	161.0(2)
O(2)–V(1)–O(4)	85.6(1)	O(9)–V(2)–O(11)	81.0(1)
O(2)–V(1)–O(1)	82.0(1)	O(9)–V(2)–O(12)	155.6(2)
O(2)–V(1)–N(1)	91.3(2)	O(9)–V(2)–N(3)	91.7(2)
O(5)–V(1)–O(4)	74.7(1)	O(12)–V(2)–O(11)	75.0(1)
O(5)–V(1)–N(1)	92.1(2)	O(12)–V(2)–N(3)	88.7(2)
O(7)–V(1)–O(2)	105.4(2)	O(14)–V(2)–O(11)	171.5(2)
O(7)–V(1)–O(5)	94.8(2)	O(14)–V(2)–O(8)	103.9(2)
O(7)–V(1)–O(4)	168.4(2)	O(14)–V(2)–O(9)	106.1(2)
O(7)–V(1)–O(1)	100.2(2)	O(14)–V(2)–O(12)	98.2(2)
O(7)–V(1)–N(1)	93.3(2)	O(14)–V(2)–N(3)	95.0(2)
N(1)–V(1)–O(4)	82.5(2)	N(3)–V(2)–O(11)	79.9(2)

Table S7. Selected bond distances (Å) and angles (°) for [Λ,Λ-$V^{IV}_2O_2$(*R*,*R*-tart)$(Him)_6$]·$4H_2O$ (**2**).

2			
V(1)–O(1)	1.975(2)	V(2)–O(5)	1.976(2)
V(1)–O(2)	2.159(2)	V(2)–O(6)	2.112(2)
V(1)–O(4)	1.608(2)	V(2)–O(8)	1.618(2)
V(1)–N(1)	2.143(2)	V(2)–N(7)	2.122(2)
V(1)–N(3)	2.111(2)	V(2)–N(9)	2.102(2)
V(1)–N(5)	2.118(3)	V(2)–N(11)	2.103(2)
O(1)–V(1)–O(2)	77.61(8)	O(5)–V(2)–O(6)	78.43(8)
O(1)–V(1)–N(3)	160.48(9)	O(5)–V(2)–N(9)	161.11(9)
O(1)–V(1)–N(1)	92.24(9)	O(5)–V(2)–N(11)	92.22(9)
O(1)–V(1)–N(5)	90.52(9)	O(5)–V(2)–N(7)	89.43(9)
O(4)–V(1)–O(1)	101.77(9)	O(6)–V(2)–N(7)	85.11(9)
O(4)–V(1)–O(2)	178.0(1)	O(8)–V(2)–O(6)	177.9(1)
O(4)–V(1)–N(3)	97.5(1)	O(8)–V(2)–O(5)	102.32(9)
O(4)–V(1)–N(1)	92.6(1)	O(8)–V(2)–N(9)	96.6(1)
O(4)–V(1)–N(5)	94.8(1)	O(8)–V(2)–N(11)	94.8(1)
N(3)–V(1)–O(2)	83.22(9)	O(8)–V(2)–N(7)	93.0(1)
N(3)–V(1)–N(1)	89.9(1)	N(9)–V(2)–O(6)	82.74(9)
N(3)–V(1)–N(5)	84.9(1)	N(9)–V(2)–N(11)	85.4(1)
N(1)–V(1)–O(2)	85.56(9)	N(9)–V(2)–N(7)	90.4(1)
N(5)–V(1)–O(2)	87.15(9)	N(11)–V(2)–O(6)	87.12(9)
N(5)–V(1)–N(1)	171.47(9)	N(11)–V(2)–N(7)	171.6(1)

Table S8. Selected bond distances (Å) and angles (°) for $(H_2im)_2[\Lambda,\Delta\text{-}V^{IV}_2O_2(S,S\text{-}H_2tart)(S,S\text{-}tart)(Him)_2]\cdot Him$ (**3**).

3			
V(1)–O(1)	2.314(2)	V(2)–O(8)	1.991(2)
V(1)–O(2)	2.011(2)	V(2)–O(9)	2.056(2)
V(1)–O(4)	1.964(2)	V(2)–O(11)	2.146(2)
V(1)–O(5)	1.994(2)	V(2)–O(12)	1.995(2)
V(1)–O(7)	1.603(2)	V(2)–O(14)	1.605(2)
V(1)–N(1)	2.118(2)	V(2)–N(3)	2.129(2)
O(2)–V(1)–O(1)	75.12(7)	O(9)–V(2)–O(8)	75.21(7)
O(2)–V(1)–N(1)	88.53(9)	O(9)–V(2)–N(3)	92.42(8)
O(4)–V(1)–O(1)	81.39(7)	O(11)–V(2)–O(9)	90.11(7)
O(4)–V(1)–O(5)	81.26(8)	O(11)–V(2)–O(8)	85.02(7)
O(4)–V(1)–O(2)	90.30(8)	O(11)–V(2)–N(3)	165.89(9)
O(4)–V(1)–N(1)	160.38(9)	O(12)–V(2)–O(9)	159.71(8)
O(5)–V(1)–O(1)	80.85(7)	O(12)–V(2)–O(8)	85.51(7)
O(5)–V(1)–O(2)	155.48(8)	O(12)–V(2)–O(11)	81.88(7)
O(5)–V(1)–N(1)	91.83(9)	O(12)–V(2)–N(3)	91.13(8)
O(7)–V(1)–O(1)	171.50(9)	O(14)–V(2)–O(12)	105.32(9)
O(7)–V(1)–O(4)	104.04(9)	O(14)–V(2)–O(9)	94.38(9)
O(7)–V(1)–O(5)	106.3(1)	O(14)–V(2)–O(8)	168.53(9)
O(7)–V(1)–O(2)	98.1(1)	O(14)–V(2)–O(11)	100.02(9)
O(7)–V(1)–N(1)	95.5(1)	O(14)–V(2)–N(3)	93.6(1)
N(1)–V(1)–O(1)	79.39(9)	N(3)–V(2)–O(8)	82.21(9)

Table S9. Selected bond distances (Å) and angles (°) for [Δ,Δ-$V^{IV}_2O_2$(*S*,*S*-tart)$(Him)_6$]·$4H_2O$ (**4**).

4			
V(1)–O(1)	1.977(4)	V(2)–O(5)	1.966(4)
V(1)–O(2)	2.114(4)	V(2)–O(6)	2.160(4)
V(1)–O(4)	1.615(4)	V(2)–O(8)	1.596(4)
V(1)–N(1)	2.127(5)	V(2)–N(7)	2.148(5)
V(1)–N(3)	2.091(5)	V(2)–N(9)	2.125(5)
V(1)–N(5)	2.105(5)	V(2)–N(11)	2.126(5)
O(1)–V(1)–O(2)	78.3(2)	O(5)–V(2)–O(6)	77.6(2)
O(1)–V(1)–N(3)	161.2(2)	O(5)–V(2)–N(7)	92.2(2)
O(1)–V(1)–N(5)	92.4(2)	O(5)–V(2)–N(9)	160.7(2)
O(1)–V(1)–N(1)	89.6(2)	O(5)–V(2)–N(11)	90.6(2)
O(2)–V(1)–N(1)	85.3(2)	O(8)–V(2)–O(5)	101.56(2)
O(4)–V(1)–O(2)	178.1(2)	O(8)–V(2)–O(6)	178.0(2)
O(4)–V(1)–O(1)	102.3(2)	O(8)–V(2)–N(7)	92.7(2)
O(4)–V(1)–N(3)	96.4(2)	O(8)–V(2)–N(9)	97.5(2)
O(4)–V(1)–N(5)	95.0(2)	O(8)–V(2)–N(11)	94.5(2)
O(4)–V(1)–N(1)	92.9(2)	N(7)–V(2)–O(6)	85.6(2)
N(3)–V(1)–O(2)	82.9(2)	N(9)–V(2)–O(6)	83.4(2)
N(3)–V(1)–N(5)	85.5(2)	N(9)–V(2)–N(7)	90.0(2)
N(3)–V(1)–N(1)	89.9(2)	N(9)–V(2)–N(11)	84.7(2)
N(5)–V(1)–O(2)	86.8(2)	N(11)–V(2)–O(6)	87.3(2)
N(5)–V(1)–N(1)	171.3(2)	N(11)–V(2)–N(7)	171.6(2)

Table S10a. The formulas of oxidovanadium tartrates **1** – **18**, other oxidovanadium hydroxycarboxylates **19** – **38** and reported FeV-cos **39** – **43**.

Complexes (V^{n+})	Formulas
1(+4)	$(H_2im)_2[\Delta,\Lambda\text{-}V^{IV}{}_2O_2(R,R\text{-}H_2tart)(R,R\text{-}tart)(Him)_2]\cdot Him$
2(+4)	$[\Lambda,\Lambda\text{-}V^{IV}{}_2O_2(R,R\text{-}tart)(Him)_6]\cdot 4H_2O$
3(+4)	$(H_2im)_2[\Lambda,\Delta\text{-}V^{IV}{}_2O_2(S,S\text{-}H_2tart)(S,S\text{-}tart)(Him)_2]\cdot Him$
4(+4)	$[\Delta,\Delta\text{-}V^{IV}{}_2O_2(S,S\text{-}tart)(Him)_6]\cdot 4H_2O$
5[1](+4)	$(NH_4)_4[V_2O_2(tart)_2]\cdot 2H_2O$
6[2](+4)	$Na_4[V_2O_2(tart)_2]\cdot 12H_2O$
7[3](+4)	$Rb_4[V_2O_2(tart)_2]\cdot 2H_2O$
8[3](+4)	$Cs_4[V_2O_2(tart)_2]\cdot 2H_2O$
9[4](+4)	$Ca_2[V_2O_2(tart)_2]\cdot 8H_2O$
10[5](+4)	$(NEt_4)_4[V_2O_2(tart)_2]\cdot 8H_2O$
11[6](+4)	$Cs_2[V_2O_2(H_2tart)(tart)(H_2O)_2]\cdot 2H_2O$
12[6](+4)	$Rb_2[V_2O_2(H_2tart)(tart)(H_2O)_2]\cdot 2H_2O$
13[6](+4)	$K_2[(VO)_2(tart)_2(H_2O)_2]\cdot 2H_2O$
14[6](+4)	$[Na_2(H_2O)_5V_2O_2(H_2tart)(tart)]\cdot 2H_2O$
15[7](+4)	$[VO(O_2)(bpz^*eaT)\cdot VO(H_2tart)]\cdot H_2O$
16[8](+5)	$(NMe_4)_2[V_2O_4(R,R\text{-}H_2tart)_2]\cdot 6H_2O$
17[8](+5)	$(NMe_4)_2[V_2O_2(R,R\text{-}tart)(S,S\text{-}tart)]$
18[8](+5)	$(NEt_4)_2[V_2O_2(R,R\text{-}tart)(S,S\text{-}tart)]$
19[9](+4)	$[VO(Hglyc)(phen)(H_2O)]Cl\cdot 2H_2O$
20[9](+4)	$[VO(glyc)(bpy)(H_2O)]$
21[9](+4)	$(NH_4)_2[VO(glyc)(Hglyc)_2]\cdot H_2O$
22[10](+4)	$K_3[V_2O_2(Hcit)(cit)]\cdot 7H_2O$
23[10](+4)	$Na_4[V_2O_2(cit)_2]\cdot 12H_2O$
24[10](+4)	$(NH_4)_4[V_2O_2(cit)_2]\cdot 2H_2O$
25[11](+4)	$[VO(H_2cit)(bpy)]\cdot 2H_2O$
26[11](+4)	$[VO(H_2cit)(phen)]\cdot 1.5H_2O$
27[11](+4)	$[VO(H_2cit)(phen)]_2\cdot 6.5H_2O$
28[12](+4)	$[VO(H_2cit)(bpy)]\cdot 1.5H_2O$
29[13](+5)	$Na_2[V_2O_4(H_2cit)_2]\cdot 2H_2O$
30[14](+5)	$(NH_4)_4[V_2O_4(Hcit)_2]\cdot 4H_2O$
31[14](+5)	$(NH_4)_6[V_2O_4(cit)_2]\cdot 6H_2O$
32[15](+5)	$[V_2O_3(phen)_3(Hcit)]\cdot 5H_2O$
33[15](+5)	$[V_2O_3(phen)_3(Hcit)_2(phen)_3O_3V_2]\cdot 12H_2O$
34[15](+5)	$[V_2O_3(phen)_3(R,S\text{-}H_2homocit)]Cl\cdot 6H_2O$
35[16](+5)	$K_2[V_2O_4(R,S\text{-}H_2homocit)_2]\cdot 6H_2O$
36[16](+3)	$[\Delta\text{-}V^{III}{}_4V^{IV}{}_4O_5(R\text{-}mal)_6(Hdatrz)_6]\cdot 44.5H_2O$
37[16](+3)	$[\Lambda\text{-}V^{III}{}_4V^{IV}{}_4O_5(S\text{-}mal)_6(Hdatrz)_6]\cdot 38.5H_2O$
38(+3)	$K_7[V^{III}{}_5V^{IV}{}_3O_5(R,S\text{-}mal)_6(trz)_6]\cdot 17H_2O$

FeV-co in nitrogenases	
39[17](+3)	$VFe_7S_8C(CO_3)$[*R*-(H)homocit] [PDB *5N6Y*]
40[18](+3)	$VFe_7S_7C(CO_3)(OH)$[*R*-(H)homocit] [PDB *6FEA*]
41[19](+3)	$VFe_7S_8C(CO_3)$[*R*-(H)homocit] [PDB *7ADR*]
42[19](+3)	$VFe_7S_7C(CO_3)$[*R*-(H)homocit] [PDB *7ADY*]
43 (+3)	$VFe_7S_7C(CO_3)$(μCO)(tCO)[*R*-(H)homocit] [PDB *7AIZ*]

Abbreviation: bpz*eaT = 2,4-bis(3,5-dimethyl-1H-pyrazol-1-yl)-6-diethylamino-1,3,5-triazine; av = average

Table S10b. Comparisons of selected bond distances (Å) for oxidovanadium tartrates **1** – **18**, other oxidovanadium hydroxycarboxylates **19** – **38** and reported FeV-cos **39** – **43**.

Complexes (V^{n+})	V–O α-alkoxy	V–O α-hydroxy	V–O α-carboxy	$V–N_{im}$	C–O α-alkoxy	C–O α-hydroxy
1(+4)	1.975(3)$_{av}$	2.237(3)$_{av}$	2.009(4)$_{av}$	2.128(4)$_{av}$	1.413(6)$_{av}$	1.418(6)$_{av}$
2(+4)	1.976(2)$_{av}$		2.136(2)$_{av}$	2.117(3)$_{av}$	1.400(3)$_{av}$	
3(+4)	1.980(2)$_{av}$	2.230(2)$_{av}$	2.013(2)$_{av}$	2.124(2)$_{av}$	1.411(3)$_{av}$	1.418(3)$_{av}$
4(+4)	1.972(4)$_{av}$		2.137(4)$_{av}$	2.120(5)$_{av}$	1.406(6)$_{av}$	
5[1](+4)	1.860(2)$_{av}$		2.020(2)$_{av}$		1.435(3)$_{av}$	
6[2](+4)	1.910(6)$_{av}$		1.999(6)$_{av}$		1.409(9)$_{av}$	
7[3](+4)	1.917(2)$_{av}$		1.996(2)$_{av}$		1.401(4)$_{av}$	
8[3](+4)	1.914(2)$_{av}$		1.999(2)$_{av}$		1.412(4)$_{av}$	
9[4](+4)	1.912(1)$_{av}$		1.994(1)$_{av}$		1.408(4)$_{av}$	
10[5](+4)	1.934(3)$_{av}$		2.024(3)$_{av}$		1.392(4)$_{av}$	
11[6](+4)	1.961(2)$_{av}$	2.122(2)$_{av}$	1.999(2)$_{av}$		1.410(4)$_{av}$	1.428(4)$_{av}$
12[6](+4)	1.956(2)$_{av}$	2.238(2)$_{av}$	1.999(2)$_{av}$		1.410(3)$_{av}$	1.425(4)$_{av}$
13[6](+4)	1.970(4)$_{av}$	2.326(4)	1.990(4)$_{av}$		1.424(7)$_{av}$	1.441(7)
14[6](+4)	1.944(3)$_{av}$	2.306(3)$_{av}$	1.999(3)$_{av}$		1.416(5)$_{av}$	1.428(5)$_{av}$
15[7](+4)	1.806(3)$_{av}$		1.949(3)$_{av}$		1.396(5)$_{av}$	
16[8](+5)		2.272(2)	1.970(2)		1.426(3)	
17[8](+5)	1.825(2)$_{av}$		1.952(2)$_{av}$		1.414(2)$_{av}$	
18[8](+5)	1.820(1)$_{av}$		1.950(1)$_{av}$		1.409(2)$_{av}$	
19[9](+4)		2.231(2)	1.997(2)			1.422(4)
20[9](+4)	1.931(2)		2.018(2)		1.412(3)	
21[9](+4)	1.927(2)	2.244(2)	2.027(2)$_{av}$		1.410(4)	1.413(3)
22[10](+4)	1.976(5)$_{av}$		1.981(6)		1.424(5)$_{av}$	
23[10](+4)	2.108(2)$_{av}$		2.039(2)		1.423(2)$_{av}$	
24[10](+4)	2.077(2)$_{av}$		2.049(2)$_{av}$		1.429(2)$_{av}$	
25[11](+4)		2.197(5)	1.993(4)			1.440(8)
26[11](+4)		2.209(4)	1.983(3)			1.451(6)
27[11](+4)		2.109(6)$_{av}$	2.026(6)$_{av}$			1.433(1)$_{av}$

28[12](+4)		2.209(3)	1.994(3)			1.436(6)
29[13](+5)	2.000(3)		1.957(3)		1.424(5)	
30[14](+5)	2.026(1)$_{av}$		1.977(2)		1.422(2) $_{av}$	
31[14](+5)	1.981(2)$_{av}$		2.004(2)		1.423(2) $_{av}$	
32[15](+5)	1.851(4)		2.082(4)		1.432(8)	
33[15](+5)	1.858(1)		2.072(1)		1.410(2)	
34[15](+5)	1.858(4)		2.085(4)		1.410(7)	
35[16](+5)	1.980(8)$_{av}$		1.959(8)$_{av}$		1.463(8) $_{av}$	
36[16](+3)	1.992(4)				1.419(7)	
37[16](+3)	1.994(4)				1.404(8)	
38[16](+3)	2.005(2)$_{av}$				1.419(4)	
39[17](+3)		2.170	2.112	2.304		1.436
40[18](+3)		2.160	2.104	2.251		1.449
41[19](+3)		2.146	2.112	2.267		1.456
42[19](+3)		2.143	2.115	2.263		1.438
43[20](+3)		2.163	2.117	2.270		1.438

Table S11. Comparisons of Mo–O distances (Å) in typical molybdenum citrates with bridging sulfur/oxygen atom.

Complexes	Mo–$O_{\alpha\text{-alkoxy}}$	Mo–$O_{\alpha\text{- carboxy}}$
Mo–μ_2–S		
$K_{2.5}Na_2NH_4[Mo^V{}_2O_2S_2(cit)_2]\cdot 5H_2O$[21]	$2.021(8)_{av}$	$2.130(1)_{av}$
$K_4(NH_4)_2[Mo^V{}_2O_2S_2(cit)_2]\cdot 10H_2O$[22]	1.975(8)	2.199(9)
$K_5(NH_4)[Mo^V{}_2O_2S_2(cit)_2]\cdot CH_3OH\cdot 5H_2O$[23]	$1.994(5)_{av}$	$2.192(5)_{av}$
Mo–μ_2–O		
$(NH_4)_6[Mo^V{}_2O_4(cit)_2]\cdot 3H_2O$[24]	2.016(4)	2.152(3)

Table S12. Bond valence calculations for complexes $(H_2im)_2[\Delta,\Lambda\text{-}V^{IV}{}_2O_2(R,R\text{-}H_2tart)(R,R\text{-}tart)(Him)_2]\cdot Him$ (**1**), $[\Lambda,\Lambda\text{-}V^{IV}{}_2O_2(R,R\text{-}tart)(Him)_6]\cdot 4H_2O$ (**2**), $(H_2im)_2[\Lambda,\Delta\text{-}V^{IV}{}_2O_2(S,S\text{-}H_2tart)(S,S\text{-}tart)(Him)_2]\cdot Him$ (**3**) and $[\Delta,\Delta\text{-}V^{IV}{}_2O_2(S,S\text{-}tart)(Him)_6]\cdot 4H_2O$ (**4**), respectively.

Complexes	Atoms	N	$\sum S_{ij}$	Δ
$(H_2im)_2[\Delta,\Lambda\text{-}V^{IV}{}_2O_2(R,R\text{-}H_2tart)(R,R\text{-}tart)(Him)_2]\cdot Him$ (**1**)	V(1)	4+	4.138	0.138
	V(2)	4+	4.148	0.148
$[\Lambda,\Lambda\text{-}V^{IV}{}_2O_2(R,R\text{-}tart)(Him)_6]\cdot 4H_2O$ (**2**)	V(1)	4+	4.099	0.099
	V(2)	4+	4.162	0.162
$(H_2im)_2[\Lambda,\Delta\text{-}V^{IV}{}_2O_2(S,S\text{-}H_2tart)(S,S\text{-}tart)(Him)_2]\cdot Him$ (**3**)	V(1)	4+	4.116	0.116
	V(2)	4+	4.117	0.117
$[\Delta,\Delta\text{-}V^{IV}{}_2O_2(S,S\text{-}tart)(Him)_6]\cdot 4H_2O$ (**4**)	V(1)	4+	4.185	0.185
	V(2)	4+	4.130	0.130

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